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THE

AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

ART. I.—*The Heating Effects produced by Röntgen Rays in Different Metals, and their Relation to the Question of Changes in the Atom;* by H. A. BUMSTEAD.

THE study of the phenomena of radio-activity during the past five or six years, and, in particular, the brilliant series of experiments and deductions which we owe to Rutherford, have left little room for doubt that a certain proportion of the atoms of radio-active elements are continually breaking up, and that the constant emission of energy by these bodies is a result of this atomic disintegration. This process in any given radio-active body appears to be going on at a fixed and definite rate which is characteristic of the particular substance studied and which is quite uninfluenced by any external circumstances whatever. Although radio-active substances have been subjected to the greatest extremes of temperature available in the laboratory, and to great variations in other physical and chemical conditions, no certain results have been obtained (so far as the writer is aware) which point to any corresponding change in the rate of decay of the substance. In fact the process of atomic disintegration has appeared to be quite beyond human control.*

On the other hand, all substances when illuminated with Röntgen rays, or with Becquerel rays of the γ-type, give out a complex secondary radiation, part of which at least is wholly different in character from the primary radiation. For example, the secondary radiation due to Röntgen rays consists in part of negatively charged corpuscles or electrons which are not present in primary rays. This suggests that there may be some

* The apparent change (due to high temperature) in the rate of decay of radium-excited activity, discovered by Curie and Danne, has been shown to be due to the fact that the successive products of radium volatilized at different temperatures. Cf. Bronson, this Journal, July 1905.

breaking up of the atom of the secondary radiator; but it is only a suggestion, for it by no means follows that the presence of β-rays involves atomic disintegration. The modern theories of electrical conduction imply the existence in conductors (and all bodies are conductors to a greater or less extent) of large numbers of corpuscles not closely bound up in the atomic structure; and it is quite conceivable that some of these may constitute the secondary β-rays, the necessary energy having been, in some way, imparted to them by the primary radiation. The most direct way of descriminating between these two possibilities is to investigate the energy relations when, for example, Röntgen rays are absorbed by matter. If none of the atoms are broken up, then the conservation of energy, in the ordinary sense, will hold; if, on the other hand, some of the atoms are exploded by the Röntgen rays, as dynamite is exploded by a shock, then the total energy after the absorption of the rays may be considerably greater than the energy of the rays themselves. This excess of energy might be expected to manifest itself mainly in the form of heat in the absorbing body; for it is known that a large fraction of the secondary Röntgen rays are very easily absorbed indeed;* and Sagnac found that tertiary rays were more easily absorbed than secondary rays.† Thus only the secondary rays which are produced very near the surface of the absorber would carry their energy away with them; those which are set up thoughout the mass of the body would be absorbed before reaching the surface, and eventually would warm the absorber.

Assuming for the moment that Röntgen rays are able to cause atoms to break up, it is very improbable that the atoms of different substances are equally susceptible to this effect; and we should expect to find an inequality in the amount of heat produced when Röntgen rays are equally absorbed in different substances. If, on the contrary, there is no atomic disintegration, the quantities of heat should be equal. It was from this point of view that the problem was proposed to me by Professor J. J. Thomson, during my stay in Cambridge last year, and the experiments which I am about to describe were carried out in the Cavendish Laboratory under his direction, and owe much to his advice and coöperation.

In considering the various experimental means by which this problem could be attacked, the radiometer seemed to promise certain advantages over other heat-measuring instruments. For measuring ordinary radiation with this instrument (the development of which is chiefly due to E. F. Nichols) the usual method is to have opaque vanes with a transparent wall near

* J. J. Thomson: The Conduction of Electricity through Gases, p. 263.
† Ibid. p. 273.

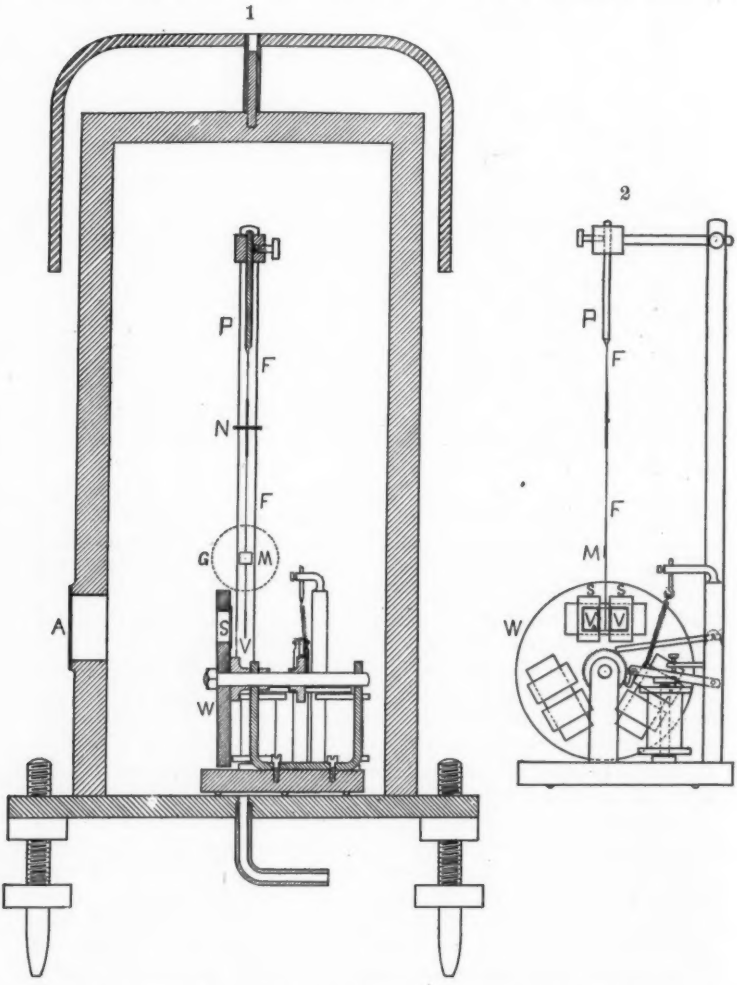
them upon one side; when one of the vanes is illuminated, it is heated, and the molecular reaction causes it to be repelled from the neighboring wall. But it is quite possible to reverse this procedure and have the wall opaque and the vanes transparent, and, although the attainable sensitiveness is probably less than in the other case, it has obvious advantages when one is dealing with Röntgen rays instead of ordinary light. The walls can be made of the metals under investigation, and of suitable thickness to absorb a considerable fraction of the rays incident upon them; while the vanes may be made very transparent to the rays and be thus far less in the way, and be less heated by the rays (independently of the heating of the substances under examination) than would be possible with the thermopile or bolometer. In the construction of the radiometer and its gradual adaptation to the present purpose, I was particularly fortunate in having the advice and assistance of Professor E. F. Nichols, who was also in Cambridge, and who most kindly put at my disposal the results of his long experience with the radiometer. I wish here to express my thanks to him for a much shorter period of apprenticeship to the instrument than would have been possible without his help.

Apparatus.

The radiometer and its adjuncts passed through many preliminary and tentative forms before a satisfactory arrangement was obtained. The final form, which proved fairly sensitive and manageable, is here described.

The vanes were made of aluminium foil which weighed about 1^{mg} per sq. centimeter. Each vane measured 8×10 millimeters with its greatest dimension vertical, and the two pieces of foil were stretched between two very thin horizontal rods of glass at top and bottom, which in turn were kept at the proper distance apart by their attachments to the central rod of the suspended system. The inner edges of the vanes were 4^{mm} apart. The various joints were made by very small drops of alcoholic shellac, which were baked on with a hot glass rod. The system was put together on a flat brass table and, after a few trials, it was not difficult to get one in which the aluminium vanes were very fairly smooth, plane, and parallel to the central rod. The mirror, for use with telescope and scale, was attached to the central rod 3^{cm} above the middle of the vanes; it was usually about 5^{mm} square and was made of specially selected microscope cover glass. All the mirrors used gave very satisfactory definition. In the final system the weight of the mirror was .13 milligrams, that of the rest of the suspended system 5 milligrams; the moment of inertia was

approximately 0·002 grm. cm². The two aluminium vanes were electrically connected by means of a bit of light phosphor-bronze strip. The other details of the suspension are shown



in figs. 1 and 2. The working quartzfiber, F, is 3^{cm} long, and is suspended from a glass rod carrying a small magnetic needle, N: as this, in turn, is suspended by a second fiber, F′, it may be caused to rotate by means of the bent magnet out-

side the case; it thus serves as a sort of torsion head for controlling the zero of the radiometer. This very elegant device is borrowed from the work of Nichols and Hull on the pressure of radiation.

The metals whose heating effects were to be compared were mounted upon an ebonite disc (W, figs. 1 and 2) 6^{mm} thick and $7{\cdot}8^{cm}$ in diameter. Three rectangular holes, $3{\cdot}6 \times 1{\cdot}4^{cm}$, were cut in this disc, at an angular distance from each other of 120°. Across these holes strips of the metals under investigation were fastened with a little soft wax; the strips were 2^{cm} long and 1^{cm} wide and their inner edges were 4^{mm} apart. Up to the present, I have had time to compare only two metals, lead and zinc. The lead strips were $0{\cdot}30^{mm}$ thick and the zinc strips $0{\cdot}82^{mm}$, these thicknesses being chosen because they gave nearly the same absorption of the Röntgen rays used, as will appear later. The thinner lead strips were blocked up from the wheel on small bits of card, so that the surface of lead and zinc toward the radiometer vanes were in the same plane. The arrangement of the metal strips on the ebonite disc was as follows: across one of the rectangular openings two lead strips were placed; this was for testing the balance of the radiometer when both vanes were influenced by the same metal; across the second opening a lead and a zinc strip were placed side by side, while the third opening also contained a lead and a zinc strip but in reversed order. The shaft which carried the ebonite disc was provided with a ratchet wheel with sixty teeth; and the disc could be rotated from one position to another by an electromagnet inside the radiometer case. The current for this purpose was led in by means of wires passing through small glass tubes sealed with sealing-wax, into holes in the base-plate of the instrument. Certain marks on the edge of the ebonite disc which could be seen through the observing window enabled one to be sure that the disc was in proper position in any given case. All the metal strips, before being mounted on the disc, were covered on both sides with leaf aluminium, which was held by the thinnest possible layer of soft wax, put on when the metal was hot. This was to give both metals the same surface, so that the loss of heat from the surface for a given rise in temperature might be the same in both cases. The ebonite disc was also covered with aluminium leaf to avoid electrostatic effects; to the same end a small quantity of an impure radium salt was put inside the case in a small open dish. All the metal strips were connected to the shaft of the wheel by thin copper wires; the shaft in turn was connected to the case and to earth.

The portions of the apparatus hitherto described stood upon a brass base-plate turned flat and smooth, which rested on

three levelling screws. Through this plate passed the tube which led to the P_2O_5 bulb, pump, and McLeod gauge. The whole was covered with a heavy, cylindrical, brass casting, $12{\cdot}5^{cm}$ in internal diameter, 29^{cm} high, and with walls $1{\cdot}4^{cm}$ thick. This heavy metal case was found to be necessary owing to the sensitiveness of the radiometer to thermal disturbances; with a blackened glass bell-jar, which was first tried, the zero was so unsteady that nothing could be done with the instrument. As a further protection against thermal disturbance, the cover and base were surrounded with cotton-wool and a felt jacket drawn over the whole. The case was provided with two windows, $2{\cdot}9^{cm}$ in diameter; one of these (A, fig. 1) was covered with sheet aluminium $1{\cdot}2^{mm}$ thick and served to admit the beam of Röntgen rays; the other was of glass for observing the deflections. Both were put on with sealing wax and the joints covered with soft wax. The inside of the cover was painted with lampblack in alcohol, with a little shellac to make it stick. The bottom of the cover was turned flat, and the joint between it and the brass plate was surrounded by a mixture of equal parts by weight of vaseline, paraffin and rubber, which, after being put on, was glazed over with a small gas flame. When all the joints were carefully made, little difficulty was experienced in maintaining the vacuum for considerable periods; the rise in pressure due to leakage was usually less than $0{\cdot}002^{mm}$ per day.

In the preliminary experiments for testing the working conditions of the radiometer, the ebonite wheel and its metal strips were replaced by a light ebonite frame which carried two strips of platinum foil (one opposite each vane), through either of which a known current could be sent. By this means one could readily find the pressure of maximum sensitiveness, and compare different quartz fibers and different forms of the suspended system. The best pressure appeared to be between $0{\cdot}03$ and $0{\cdot}08^{mm}$, and within this region the variation of sensitiveness with pressure was slow; in the subsequent work a pressure between these two limits was usually employed. From a knowledge of the resistance of the platinum strips and of the current employed, it appeared that a deflection of one millimeter (scale distance, 196^{cm}) corresponded to an emission of about $0{\cdot}04$ ergs per second from each square centimeter of platinum surface. The deflections were also found to be proportional to the energy generated in the strips. Of course the radiometer action depends primarily on the temperature of the surface, and with a surface of different emissivity, the deflection for a given emission of energy will be different.

The Röntgen bulb finally employed was a very large one made by Müller and obtained from Isenthal & Co. The diam-

eter of its spherical portion was 17^{cm} and the electrodes were big enough to bear a very heavy discharge. The anti-cathode was sealed into the bottom of the water tube so that it was in direct contact with the water, and I have frequently caused the water in the tube to boil without seriously heating the rest of the tube. It was provided with an automatic vacuum adjuster which worked well; the focus was sharp and the Röntgen rays obtained were very powerful and fairly steady in intensity and "hardness." The bulb was driven by an 18-inch Apps coil and a rotating mercury-jet interrupter. The coil was in an adjoining room and about 6 meters from the radiometer; its orientation was adjusted so that it produced very little effect upon the magnetic "torsion head" of the instrument—less than 4^{mm} with the largest currents used; this was always in one direction and could be applied as a correction. The secondary leads were gutta-percha covered and supported by silk ribbons; where they passed from one room to the other, through the wooden frame over a door, they were enclosed in long glass tubes. As the rays used were not very hard, there was little difficulty with the insulation, though there was often a good deal of brush discharge from the leads. The earthed metallic case of the radiometer protected it completely from any electrostatic disturbance. A lead screen, 2^{mm} thick, which hung by a quadrifilar suspension from the ceiling about 2^{cm} in front of the aluminium window, permitted both strips to be exposed to the Röntgen rays, or both screened, or either exposed while the other was screened. A large cardboard screen was kept between the Röntgen bulb and the radiometer to diminish the effects upon the instrument due to the heating of the bulb.

Measurements of the absorption of the lead and zinc were carried on simultaneously with the radiometer observations. For this purpose an electroscope was set up 270^{cm} from the bulb; it had an aluminium window 2^{cm} in diameter and the remainder was covered with sheet lead 2^{mm} thick. As this did not sufficiently protect it from the rays, a lead wall was built up of blocks two inches thick between the electroscope and bulb, with a hole opposite the window; this gave satisfactory protection, when the window was screened. Observations were made with a micrometer microscope and stop-watch in the usual manner.

Experiments.

The experimental method was based upon the following considerations: the Röntgen rays absorbed in the strips will generate heat throughout the mass of the metals and a steady state of temperature will be reached when the heat generated

per second is equal to the heat lost per second through the two surfaces by radiation and convection. (The possibility of any appreciable loss by conduction through the ebonite support of the strips will be considered later.) The heat lost through any surface is proportional to its emissivity and, for such small temperature differences, to its excess of temperature above its surroundings. The lead and zinc strips had the same surface—aluminium leaf—and it is natural to assume that the emissivity is the same in both cases; this assumption, however, will be justified experimentally. Moreover, it will appear from theoretical considerations that, in the steady state, the difference in temperature between the front and back surfaces of either metal is a small fraction of the excess of its temperature above its surroundings; and this too will be confirmed experimentally. It follows therefore, that, very approximately, half the heat generated in either strip is lost through each of its two surfaces, and that the total heat generated per second will be proportional to the temperature of either surface in the steady state, and hence to the repulsion of the radiometer vane exposed to that surface.

The first step in a series of experiments was to test the balance of the radiometer by exposing the two lead strips simultaneously to the Röntgen rays. The balance was usually found to be fairly good and could be to some extent adjusted by moving the bulb horizontally before the window; the stand carrying the bulb could be moved by a horizontal screw for this purpose. In two of the series of experiments (quoted below) it was found impossible to get a good balance by moving the bulb; in these cases the lack of balance was determined and applied as a correction. The wheel was then clicked round to the second position, in which one vane of the radiometer was opposite to a lead strip and the other opposite to a zinc strip. This was a somewhat delicate operation, as each click caused a violent disturbance of the radiometer (partly magnetic and partly thermal) and it was necessary to get it under control by means of a subsidiary magnet before making another click; otherwise the vanes might have become entangled in the moving wheel and the suspension broken. After the shift from one position to another, several hours had to elapse before the radiometer was again fit for use. Several exposures to Röntgen rays were then made in which the zinc and lead strips were exposed separately and both together. The wheel was then moved to the third position, in which the zinc and lead strips were in reversed order, and similar observations taken. It may be said at once that the reversed position of the lead and zinc did not alter the character of the results.

The general nature of the results may be most readily set

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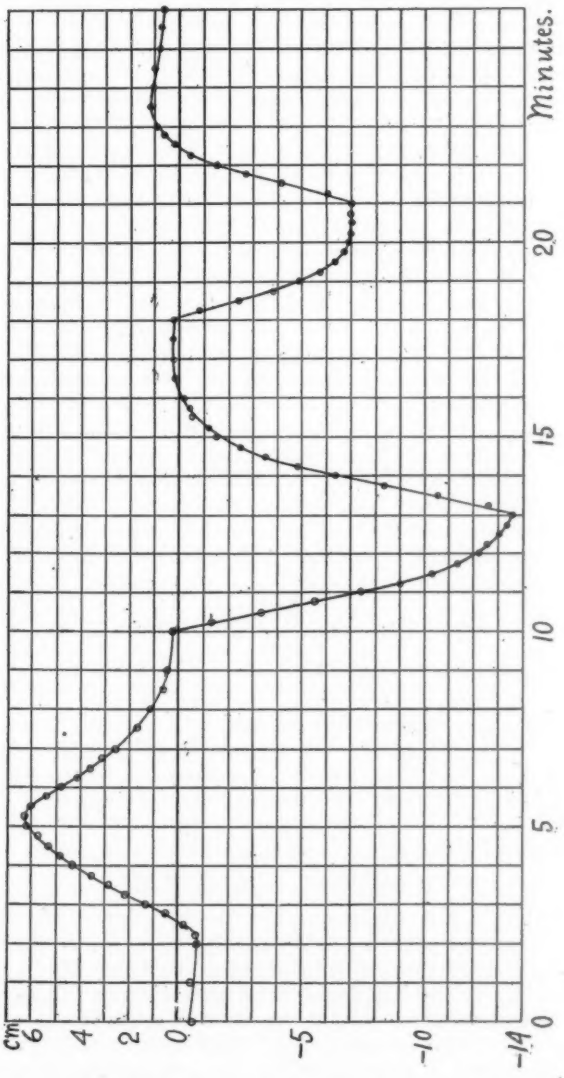

forth by considering a particular experiment as an example. In fig. 3 the results of this experiment are shown graphically;

the abscissæ represent time in minutes, the ordinates deflections of the radiometer in centimeters on the scale; the position of the wheel was such that a positive deflection means a repulsion by the zinc of its vane, a negative deflection a repulsion by the lead of its vane. Between 2^m and 5^m, the zinc strip was exposed to the rays; the rays were then cut off and the zinc allowed to cool for 5 minutes (5^m–10^m), the lead was then exposed for 3 minutes (10^m–13^m); it, in turn, was allowed to cool for 5 minutes (13^m–18^m) and then both strips exposed simultaneously for 3 minutes (18^m–21^m) after which the rays were again cut off. It is plain from the figure that neither metal was exposed long enough to the rays for the steady state to be attained; but it is also plain that the great preponderance of the lead over the zinc is not due to this cause. In fact we may from these curves get an approximate idea of what the steady deflections would have been if it had been safe to continue running the bulb at the rate necessary for such large deflections.

If λ is the coefficient of absorption of the metal for the rays used, then the energy of the rays at any point in the interior of the strip whose distance is x from the front face is $I_o e^{-\lambda x}$ and the energy absorbed in an element of thickness, dx, is $\lambda I_o e^{-\lambda x} dx$. Let us assume that the heat generated in the element is proportional to this, say $a\lambda I_o e^{-\lambda x} dx$. The equation of the flow of heat under these circumstances is:

$$c\frac{dV}{dt} = k\frac{d^2V}{dx^2} + a\lambda I_o e^{-\lambda x},$$

with the boundary conditions

$$k\left(\frac{dV}{dx}\right)_{x=o} = hV_o; \quad -k\left(\frac{dV}{dx}\right)_{x=l} = hV_l.$$

where V is the temperature (measured above the surroundings), t the time, c the specific heat of unit volume, k the conductivity, h the emissivity of the surface, and l the thickness of the strip. The solution of this will have the form

$$V = V_\infty - \Sigma A e^{-\gamma t}$$

where V_∞ is the steady value and is the solution of the differential equation with the left hand member put equal to zero; the successive values of γ in the sum are determined by a certain transcendental equation, and the A's are functions of x into which γ enters. What is observed is the temperature of the surface where $x=l$. The variation of this temperature with the time is represented fairly well (except at the very beginning) by a single term of the series of exponentials so that we may write as a rough approximation

$$V = V_\infty (1 - e^{-\gamma t}).$$

The variation of the temperature with the time during cooling will have different values of the A's and γ's, but (again excepting the initial part) the curves of heating and cooling will have very nearly the same form. This is seen in the figure, and it also appears mathematically that with the values of the conductivity and emissivity involved, there is a nearly uniform temperature throughout the metal within less than a minute after the rays are turned on. We may therefore, for such

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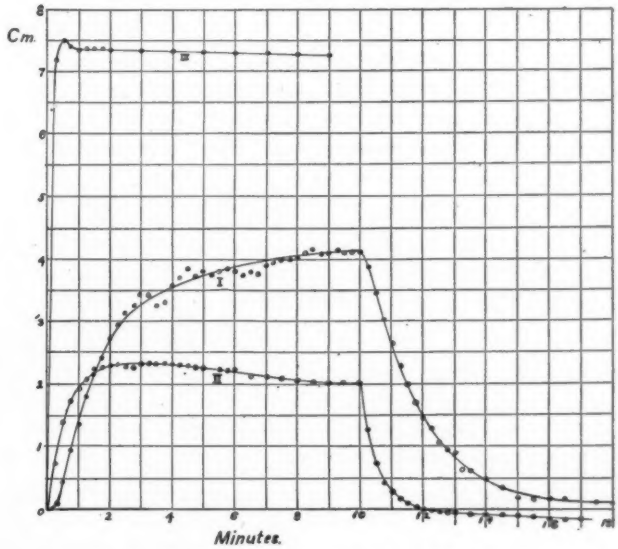

accuracy as is needed in this discussion take the curve of cooling to be represented by

$$V = V_0 e^{-\gamma t},$$

the time being counted from the moment the rays are cut off. In this equation

$$\gamma = -\frac{1}{V}\frac{dV}{dt},$$

and one may get rough values of γ for lead and for zinc by drawing tangents to the curves of cooling. In the following tables are several values found for different points of the curves in fig. 3; the zero for the zinc curve was taken as the mean of the position at 2^m and 10^m and, for lead, the mean of 10^m and 18^m.

Zinc			Lead		
V	$\frac{dV}{dt}$	γ	V	$\frac{dV}{dt}$	γ
3·0	1·8	0·6	6·0	6·2	1·0
2·0	1·6	0·8	3·0	4·0	1·3
1·5	1·05	0·7	1·5	2·5	1·7
0·8	0·50	0·6	0·8	1·3	1·6
Average		0·68	Average		1·4

In order to determine the steady value from the value at the end of three minutes we have

$$V_\infty = \frac{V}{1-e^{-\gamma t}}$$

which gives, for lead $V_\infty = 13{\cdot}95$, and for zinc $V_\infty = 7{\cdot}4$.

Approximately the same rates of cooling and heating were obtained in all the experiments made upon this point. A second example is given in figure 4, in which weaker rays were used for ten minutes instead of three. Curve I is for zinc, curve II for lead; the two experiments were made at different times and with rays of different intensity, so that the *magnitudes* of the deflection have nothing to do with each other. To show that the inertia and damping of the suspended system have no sensible effect upon the determination of the rates of heating and cooling, curve III is added for comparison. This was obtained by suddenly moving the controlling magnet at the time $t = 0$; it represents the response of the suspension to a sudden impulse. The following values for γ for zinc and lead were obtained from the cooling portions of these curves:

Zinc			Lead		
V	$\frac{dV}{dt}$	γ	V	$\frac{dV}{dt}$	γ
2·0	1·2	0·6	1·0	1·5	1·5
1·0	0·58	0·58	0·5	0·8	1·6
0·5	0·38	0·76	0·3	0·48	1·6
Average		0·65	Average		1·6

Later in the course of the experiments, the aluminium window was replaced by a one of glass and the strips heated by means of a beam of light; the result of such an experiment is shown in fig. 5 below. The following values of γ are obtained in the same manner from these curves:

Zinc			Lead		
V	$\frac{dV}{dt}$	γ	V	$\frac{dV}{dt}$	γ
4·0	2·15	0·54	4·0	5·2	1·3
2·0	1·22	0·61	2·0	2·6	1·3
1·0	0·57	0·57	1·0	1·1	1·1
Average		0 57	Average		1·23

It will be seen that the agreement is as good as could be expected from the very rough nature of the determinations.

Returning now to the experiment plotted in fig. 3 it is to be observed that the steady deflection for lead is nearly twice as great as that for zinc. The fractions of the incident rays absorbed by the two strips were determined by means of the electroscope with the pieces of metal from which the strips had been cut; the pieces of lead and zinc were placed behind a sheet of aluminium of the same thickness as the window of the radiometer. It was found that the lead absorbed 79 per cent and the zinc 78 per cent of the rays which got through the aluminium; in this particular case the spark gap in the automatic adjuster of the Röntgen bulb was $7{\cdot}5^{cm}$ long.

Thus (unless there has been some error in the experimental method or in the interpretation of the result) it appears that for practically equal absorptions of Röntgen rays in lead and in zinc, about twice as much energy is generated in the lead as in the zinc. It may be said at once that essentially the same result was obtained in all the experiments, with rays of different hardness, with both positions of the strips and with the radiometer vanes sometimes between the window and the strips, as well as in the position indicated in fig. 1. Before giving, however, the numerical results of all the experiments, it will, I think, be conducive to clearness to consider the possible sources of error (so far as they have occurred to me) and their influence upon the results.

Possible Sources of Error.

1. After it had been found that the lead strips predominated, and before the rates of heating and cooling of the strips had been worked out, an effect was observed which caused considerable perplexity. The slight drift of the zero-point due to the warming up of the room after the observer entered was found to be always in the direction indicating a repulsion from the lead; its direction reversed with the reversal of the order of the strips. As the aluminium window was the only part much exposed to changes of temperature, the effect of slightly warming it was investigated. When an incandescent lamp, or a warm soldering iron, was held six inches from the aluminium window, the radiometer was deflected away from the lead strip—at first slowly, then more and more rapidly until it went off the scale and usually bumped against the zinc strip. As this was in the same direction as the effect when both strips were exposed to the Röntgen rays, it appeared that the whole effect might be spurious. By putting the lamp about two feet away from the window, less violent effects were produced, and it was possible to follow the progress of the

deflection. This was sluggish in comparison with that produced by the rays, and (as might have been expected from varying air currents in the room) was irregular and somewhat erratic in its course. In one respect, however, the behavior was consistent; if the lamp was left glowing for one or two hours, the radiometer always returned to the neighborhood of its zero-point and staid there until the lamp was turned off. It then made another slow and wandering excursion in the

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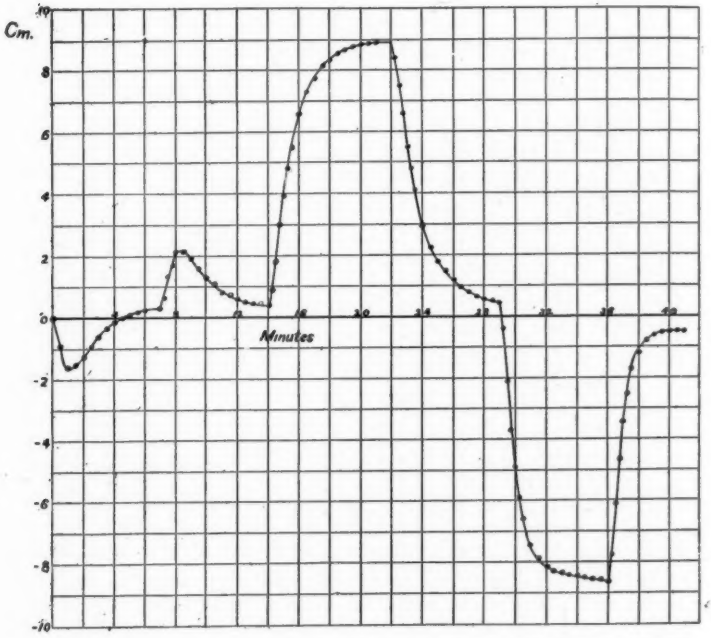

opposite direction (repulsion by zinc) and eventually again returned to the middle of the scale. The application of ice to the aluminium window also caused repulsion by the zinc.

The determination of the different rates of heating and cooling of the two strips furnished the explanation of this behavior. While the window and adjacent parts of the case are slowly warming up, they radiate to the two strips more and more, and cause the temperatures of the latter to rise steadily; but the lead having a smaller time-constant than the zinc, has the higher temperature and maintains it until the amount of radiation reaching the strips no longer varies with the time—

that is until the window has reached its stationary temperature. When this takes place the zinc has time to overtake the lead, both temperatures become the same, and the radiometer returns to zero. When the lamp is turned off and the window begins to cool, the lead cools more rapidly than the zinc and hence there is a similar deflection in the opposite direction which again lasts only so long as the temperature of the window is variable.

Although this explanation is reasonable and, in fact, inevitable, the matter here discussed touches so vitally the main conclusion of this investigation that it was desirable to test in a decisive manner the behavior of the instrument when the strips were heated by ordinary radiation. For this purpose, a glass window was substituted for the one of aluminium and (everything else being left exactly as before) a beam of light was admitted from an eight candle-power incandescent lamp, 125^{cm} from the window. The result of such an experiment is shown graphically in fig. 5, where, as before, the abscissæ represent time in minutes; the ordinates, deflections in centimeters; a positive deflection means repulsion by the zinc, a negative deflection, repulsion by lead. From 0^{m} to 7^{m} both strips were exposed to the light and the curve clearly shows the temporary deflection in favor of the lead, returning to zero as the zinc overtakes the lead; from 7^{m} to 14^{m} the window was covered by the lead screen so that both strips cooled, the zinc lagging behind as before and so giving a similar temporary deflection in the opposite direction. From 14^{m} to 22^{m}, the zinc strip was exposed while the lead was shielded, and from 29^{m} to 36^{m} the lead alone was exposed. It will be observed that the behavior is perfectly in accord with the above explanation of the heating effect, and that the deflections, when the lead and zinc are separately illuminated, are equal. The contrast with the effects of the Röntgen rays is sufficiently marked. I have exposed both strips at once to weak Röntgen rays (giving a deflection of about 2^{cm}) for 30 minutes without observing any tendency of the radiometer to return to zero.

2. At first sight, there appears to be a possibility that (on account of different heat-conductivities, etc.) one of the metals might lose more heat through the front surface and the other through the rear surface, thus giving rise to different surface temperatures, even though the quantities of heat generated were the same in both cases. A number of considerations show that this cannot account for the effects observed. It is easy to show that, when all the heat enters through the front surface, the ratio of the temperature of the front face to that of the rear face will be (when the steady state is attained)

$$\frac{V_0}{V_l} = 1 + \frac{hl}{k}$$

and the difference will be less than this when the heat is generated throughout the interior of the metals. Now a superior limit to the value of h may be readily obtained, from the rates of cooling of the strips, by assuming infinite conductivity in the metals so that the whole strip has at any instant the same temperature as the surface. Under these circumstances, we have

$$-\frac{1}{2}C\rho l\frac{dV}{dt}=hV$$

Where C is the specific heat, ρ the density and l the thickness of the metal. Also

$$-\frac{dV}{dt}=\gamma V$$

so that

$$h=\frac{1}{2}\gamma C\rho l$$

With a given curve of cooling of the surface and finite conductivity, the value of h will be less than this; because when the surface has cooled to any temperature the interior will have a higher temperature and thus not so much heat need be emitted in a given time as when the conductivity is infinite. In this way we find for the lead strip

$$h<\cdot 007$$

and for the zinc strip

$$h<\cdot 002$$

and taking $h = 0{\cdot}1$ we find, in the worst case

$$\frac{V_e}{V_l}<1{\cdot}004$$

More direct experimental evidence upon this point was obtained by reversing the position of the ebonite disc with reference to the case and putting the vanes on the side of the strips next the window instead of on the further side. The effects observed were the same as in the other position.

3. The possibility of unequal values of the emission coefficient for the aluminium-covered surfaces of the two metals is negatived by the experiments with light in which the two metals produced equal effects.

4. If much heat were lost by conduction through the ebonite support, or the copper wire by which the strips were earthed (diameter, $1/4^{mm}$), the central part of the zinc strip would be cooler than the lead on account of its greater conductivity and thickness. If this were the cause of the higher temperature of the lead it would act also when the strips are warmed by light, which is not the case. Experiments with light were

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made with the full aperture of the circular window, so that the ebonite was illuminated as well as the strips; and also with a cardboard screen in front of the window with a rectangular hole which allowed the light to fall on the strips alone and not on the ebonite. No difference was observed in the two cases.

5. The observed results cannot be due to electrostatic effects produced by the negative corpuscles of the secondary rays. The strips were earthed, and the two vanes were connected by a conductor; under these circumstances, no electrostatic effect could be produced except an instability due to *both* vanes having a different potential from the two strips. Such an instability was frequently observed after the vanes had become electrified by bumping against the strips, but no other electrical effect. Moreover, the coincidence of the rates of motion of the radiometer, when illuminated by Röntgen rays and by ordinary light, shows that the deflections produced by the rays were caused by changes of temperature and not by electrical forces.

6. The last consideration also excludes the (somewhat remote) possibility that the effect is produced by direct impact of the secondary rays.

7. It is conceivable that a slight difference in the distance of the lead and zinc strips from the vanes might cause a considerable difference in sensitiveness of the two vanes and thus account for the preponderance of the lead. If this were the case, however, the effect should have appeared in the experiments with ordinary light. I also tested the effect upon the sensitiveness of varying the vane-distance by taking deflections with the zero near the top and near the bottom of the scale. For a variation in the vane-distance of $0{\cdot}48^{mm}$ the change in sensitiveness was less than 12 per cent. The positions of the surfaces of the lead and zinc strips were afterward tested by means of a point gauge and they certainly did not differ by more than $0{\cdot}1^{mm}$.

8. It might also be imagined that the measurement of the absorptions by means of the electroscope did not give the relative amounts of energy absorbed by the lead and zinc; that the ionization in the electroscope was not a measure of the energy of the rays. One may express this possibility in slightly different form by saying that, accompanying the rays which ionize the gas, there may be other rays which do not cause ionization but which do carry energy; and that these latter may be more absorbed in the lead than in the zinc. In order to test this, measurements of the absorption were made with the radiometer itself. One strip was shielded so that as large a deflection as possible might be obtained with

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the rays and an aluminium screen of the same thickness as the window was set up in front of the window; the lead and zinc of the thickness of the strips were introduced behind this screen. The following deflections in succession were obtained by a three-minute exposure to the rays in each case:

Al	8·4
Al+Pb	0·8
Al+Zn	0·9
Al+Pb	0·6
Al	6·6

It is plain that the rays did not remain very constant during this somewhat prolonged use, but it is also plain that, whatever agent it may be which affects the radiometer, it is practically equally absorbed by the lead and the zinc. Taking the means of the readings as they stand, we find that, of the energy which gets through the aluminium, 88 per cent is absorbed by the zinc and 91 per cent by the lead.

9. Even if one assumed the substantial correctness of the energy measurements, there still remains the possibility that the difference between the two metals may not be due to atomic disintegration. It is known that secondary rays are generated by the absorption of the primary rays and it may be supposed that these carry away from the metal a considerable fraction of the energy of the primary rays—a much greater fraction in the case of zinc than in the case of lead, thus giving rise to the observed difference. An examination of this possibility is therefore necessary.

The secondary rays from such metals as lead and zinc consist of two well-defined groups, one of which is completely absorbed in less than 10^{mm} of air, the other being much more penetrating. Let us consider first the less penetrating rays. It is stated in the introductory portion of this paper that these rays must form a large fraction of all the secondary rays generated; this statement appears at first sight to be in contradiction with the experimental result obtained by H. S. Allen,* who found that the ionization produced by these easily absorbed secondary rays from brass is 1/1900 of that which would be produced by complete absorption of the primary rays in the gas. A little consideration, however, shows that, with rays so easily absorbed, a large number must be generated in the metal to permit even so small a fraction to escape.

Let the intensity of the primary rays which have penetrated a distance x into the metal be $I_1 = \bar{I}_1 e^{-\lambda_1 x}$. The absorption in an element of thickness dx will be $\lambda_1 I_1 dx$ and we may assume that this is proportional to the intensity

* Phil. Mag. iii, p. 126 (1902).

of the secondary rays (of the more absorbable type) generated in this element; say

$$I_2 dx = a\lambda_1 I_1 dx$$

The question is as to the value of the fraction a necessary to produce the observed secondary rays outside the metal. Let us assume that half of the secondary rays so generated are propagated straight back to the surface; this will give us an over-estimate of the rays which escape with a given value of a, or an under-estimate of a necessary to account for the observed secondary rays. The effect, at the surface, of the secondary rays generated in the element dx will be then

$$\frac{1}{2} I_2 dx e^{-\lambda_2 x}$$

and the total intensity of the secondary rays at the surface of the metal will be

$$\bar{I}_2 = \tfrac{1}{2}\int_0^\infty I_2 e^{-\lambda_2 x} dx = \tfrac{1}{2} a\lambda_1 \bar{I}_1 \int_0^\infty e^{-(\lambda_1+\lambda_2)x} dx$$

$$= \tfrac{1}{2} a \bar{I}_1 \frac{\lambda_1}{\lambda_1+\lambda_2}$$

The value of the coefficient of absorption in air, of the secondary rays from brass, may be obtained from Townsend's experiments* and is 6·9; he did not measure the absorption in air of the primary rays, but an estimate of its value may be got from the statement that the number of ions produced by the primary rays when they traverse a layer of air 1^{cm} thick is about half as great as the number produced by complete absorption of the secondary rays; combining this with Allen's result that complete absorption of the primary rays produced 1900 times as many ions as complete absorption of the secondary rays, we get, for the coefficient of absorption in air of the primary rays used by Townsend, approximately $3 \cdot \times 10^{-4}$. Assuming that the ratio of the coefficients of absorption in the metal is of the same order as that of the coefficients in air, we have roughly

$$\frac{\lambda_1+\lambda_2}{\lambda_1} = 2 \cdot \times 10^4$$

and as

$$\frac{\bar{I}_2}{\bar{I}_1} = \frac{1}{2000}$$

we get

$$a = 10.$$

* Camb. Phil. Soc. Proc., x, p. 217 (1899).

Now if the conclusion, toward which the present experiments point, be accepted, it is not surprising that the "fraction" a should be greater than unity; for if atomic energy is set free it is not unlikely that it is through the mechanism of these easily absorbed secondary rays. Of course the data from which the above calculation has been made are not sufficiently accurate to give any weight to the actual number obtained for a; but it is sufficiently clear that a considerable number of these easily absorbed secondary rays must be generated, of which only a very small fraction can escape from the metal.

This conclusion in itself makes it somewhat improbable that a large part of the energy could be transformed into the *more* penetrating secondary rays and so carried away; but it is desirable to consider the question of this type of rays independently. Sagnac, who has made an extensive series of experiments upon secondary rays* finds that heavier metals in general give out more intense, and more easily absorbed, rays (of the type now under consideration) than lighter metals; and, in particular, that this is true of lead as compared with zinc. On the other hand, Townsend (loc. cit.) finds that lead is an exception among the heavier metals and, as a matter of fact, gives out less intense and more penetrating rays (of this type) than zinc, and this result has recently been confirmed by Eve†. If Sagnac's result were true in general, it would of course dispose of all possibility of explaining the present experiments by means of the energy of the secondary rays; and even from Townsend's observations (when allowance is made for the difference of absorption by air) it is impossible to conclude that the total ionizing power of the secondary rays from zinc is much greater than (or even as great as) that of the rays from lead. But leaving these results out of account, I think it is possible to show that, with the rays which I used and under the experimental conditions, it is not possible to attribute the results obtained to this cause.

The secondary rays from metals are always more easily absorbed than the primary rays which generate them. Barkla‡ has shown that the secondary radiation from gases and light solids is practically identical in character with the primary radiation; and this had previously been found to be the case for such substances as paraffin by Sagnac (loc. cit.). But all experimenters, so far as I am aware, are agreed that the secondary radiation from lead, zinc and other similar metals is less penetrating than the primary; and no evidence has been obtained of any secondary rays more penetrating than the rays

* Ann. Chim. Phys., xxii, p. 493, 1901.
† Phil. Mag., viii, p. 674, 1904.
‡ Proc. Roy. Soc., lxxiv, p. 474, 1905.

which produce them. Thus if λ_1 and λ_2 are the coefficients of absorption in zinc of the primary and secondary rays respectively, we have

$$\lambda_2 > \lambda_1$$

Now in the experiment described at length above, the absorption by the zinc strip was about 0·8; the two-tenths observed behind the zinc included not only the primary rays which got through but also some of the more penetrating secondary rays from the rear surface. Hence $e^{-\lambda_1 l} < 0{\cdot}2$, and as $l = 0{\cdot}08^{cm}$

$$\lambda_2 > \lambda_1 > 20.$$

If we assume, as before, that one-half of the secondary rays generated in any element are propagated straight back toward the front surface (which will exaggerate the intensity of the secondary rays), we get for the intensity of the secondary rays escaping from the front surface

$$\bar{I}_2 < \tfrac{1}{2} a \bar{I}_1 \frac{\lambda_1}{\lambda_1 + \lambda_2} \left(1 - e^{-(\lambda_1 + \lambda_2) l}\right)$$

Writing this

$$\tfrac{1}{2} a \bar{I}_1 \lambda_1 l \frac{1 - e^{-(\lambda_1 + \lambda_2) l}}{(\lambda_1 + \lambda_2) l}$$

the fraction is seen to be of the form

$$\frac{1 - e^{-x}}{x}$$

which (for positive values of x) increases as x diminishes. Hence

$$\bar{I}_2 < \tfrac{1}{4} a \bar{I}_1 \left(1 - e^{-40 l}\right)$$

The primary rays absorbed in the zinc strip

$$A_1 = \bar{I}_1 \left(1 - e^{-\lambda_1 l}\right) > \bar{I}_1 \left(1 - e^{-20 l}\right); \text{ hence}$$

$$\frac{\bar{I}_2}{A_1} < \tfrac{1}{4} a \frac{1 - e^{-40 l}}{1 - e^{-20 l}} = \tfrac{1}{4} a \left(1 + e^{-20 l}\right); \text{ or } \frac{\bar{I}_2}{A_1} < 0{\cdot}3\, a$$

in which of course, if there is to be no generation of fresh energy, a must be less than unity.

We may make a similar calculation for the rear surface, but it is sufficient to observe that even if all the effect observed behind the metal is due to secondary rays, the ratio of these to the primary rays absorbed cannot be greater than 0·2. So that by considerably exaggerating all possibilities in favor of the production and escape of secondary rays we are unable to give to the secondary rays which escape an intensity one-half as great as that of the primary rays absorbed. Now in order

to account in this way for the observed difference in the heating of the lead and the zinc, we must assume that at least half of the energy of the primary rays absorbed in the zinc escapes in the form of secondary rays; this is on the supposition that none so escapes from the lead; if the lead loses any energy in this manner then the fraction for the zinc must be greater than one-half. It appears therefore that the experimental results cannot be accounted for in this way.

Numerical Results.

The measurements of the absorptions of lead and zinc ran so nearly parallel throughout the course of the experiments, with rays differing considerably in penetration, that it was eventually considered unnecessary to make a separate correction to each measurement with the radiometer. The absorptions were measured from time to time during the investigation and the results are given in the following table; the numbers give the fractions of the primary rays absorbed by aluminium of the same thickness as the window, and by lead and zinc of the same thickness as the strips, the latter being behind the aluminium except in the first three experiments when no aluminium was interposed. The last experiment in the table is the one made with the radiometer instead of the electroscope.

Exp.	Absorptions, Al	Pb	Zn	$\frac{\text{Pb}}{\text{Zn}}$
I	---	0·925	0·924	1·001
II	---	0·926	0·920	1·007
III	---	0·944	0·947	0·997
IV	0·57	0·862	0·856	1·007
V	0·45	0·790	0·780	1·013
VI	0·47	0·830	0·803	1·034
VII	0·45	0·809	0·805	1·005
VIII	0·31	0·684	0·684	1·000
IX	0·34	0·676	0·648	1·043
X	0·32	0·675	0·655	1·031
XI	---	0·907	0·880	1·030
		Average		1·016

The average value of the ratio is applied as a correction in the energy measurements below.

The energy measurements are given in the following table. Column I gives the time of exposure of the strips in minutes. Columns II and III give the deflections in centimeters, produced by exposure of the lead and zinc respectively. These are the observed deflections, corrected for the effect of the induction coil upon the magnetic "torsion head"; this was always

down-scale and varied from 0·1 to 0·3^{cm}; it was determined each time by allowing the coil to run with the lead screen in front of the window of the radiometer. The plus and minus signs indicate the direction of the deflection; thus a change of sign in either column represents a shift of the wheel, so that the positions of the strips are interchanged. Columns IV and V contain the deflections corrected for lack of balance of the radiometer. In experiments 1, 2, 3 and 9, the radiometer was sensibly balanced when tested by the two lead strips; in 4, 5 and 6, there was a lack of balance of 15 per cent in the positive direction; in 7 and 8 the lack of balance was 10 per cent in the same direction. Accordingly, in the first case the positive deflections (zinc) are reduced 15 per cent, in the second case the positive deflections (lead) are reduced 10 per cent. The changes in the conditions are explained by the fact that between the groups of experiments mentioned the radiometer, for one reason or another, had to be taken down and readjusted.

Columns VI and VII contain the deflections reduced to the steady state, by dividing by $(1-e^{-\gamma t})$. The values of γ used were, for lead 1·5, for zinc 0·67. Column VIII contains the ratios of VI to VII; it is the ratio of the heat generated per second in the lead strip to that generated in the zinc strip.

The first three experiments were made with the vanes between the window and the strips; the last six with the strips between the window and the vanes.

Exp.	I	II	III	IV	V	VI	VII	VIII
1	1·5	−3·45	+1·30	....	....	−3·85	+2·06	1·87
2	1·5	−6·84	+2·26	....	....	−7·65	+3·58	2·13
3	1·5	+5·20	−1·90	....	....	+5·82	−3·01	1·93
4	1·5	−5·51	+2·43	....	+2·16	−6·18	+3·41	1·81
5	1·5	−6·67	+2·64	....	+2·25	−7·46	+3·55	2·10
6	1·5	−7·07	+2·96	....	+2·51	−7·90	+3·96	2·00
7	1·5	+7·09	−2·30	+6·39	....	+7·12	−3·63	1·96
8	1·5	+9·76	−3·21	+8·80	....	+9·85	−5·07	1·94
9	3·0	−13·75	+6·4	....	....	−13·95	+7·40	1·88

The average of the ratios in Column VIII is 1·96; reducing to equal absorptions, we get, as the result of these measurements, that when Röntgen rays are equally absorbed in lead and in zinc, the quantity of heat generated in the lead is 1·93 times the quantity generated in the zinc.

The necessity of the writer's returning to America has temporarily interrupted this investigation. Further experiments are, however, now under way in which other metals will be compared, and the experimental conditions varied as

much as possible. An attempt will be made to detect the effect with a thermopile as well as with the radiometer; and to ascertain whether cathode rays produce similar effects, as might be expected. If the present results are due to some hitherto unsuspected source of error, it is hoped that the error may reveal itself as the conditions are varied.

It is in no perfunctory spirit that I wish to express my thanks to Professor J. J. Thomson for permission to work in the Cavendish Laboratory and for the help which I constantly derived from his advice and suggestions, some of which were vital to the success of the experiments. I take pleasure in acknowledging my great indebtedness to him.

Conclusions.

The present experiments indicate that when Röntgen rays are equally absorbed in lead and in zinc, approximately twice as much heat is generated in the lead as in the zinc. It does not appear possible to attribute this result to errors in the measurements or in the theory underlying the experimental method.

To account for this effect the writer has been able to think of only one hypothesis which is not in more or less direct conflict with experimental facts. This hypothesis is that, by means of Röntgen rays, the atoms of certain elements may be artificially broken up and that the energy thus liberated forms a part (and perhaps the greater part) of the energy which appears when the rays are absorbed by matter.

New Haven, Conn., Oct. 20, 1905.

ART. II.—*On a Method of Determining the Specific Gravity of Soluble Salts by Displacement in their own Mother-liquor; and its Application in the case of the Alkaline Halides;** by J. Y. BUCHANAN.

DURING the summer of 1904 I was occupied with the determination of the specific gravity of various saline solutions by the hydrometric method, which I designed for use on board the "Challenger" and have perfected in the course of years, since that date. The most important condition of success with this method is to operate always at the same temperature, and during an operation to keep that temperature perfectly constant. The temperature which I used was 19·5°, both because a great quantity of similar work has been done at this temperature and because, in the room which it was my privilege to occupy in the Davy-Faraday Laboratory, this temperature is one which is very easily produced and kept constant, so long as the temperature of the air outside does not exceed it. This work was put a stop to by the arrival of the great anticyclone of the summer of 1904 which persisted over northern Europe for nearly six weeks and produced tropical conditions, which were evidenced alike by the high temperature of the air and by its insignificant diurnal variation.

In these circumstances I decided to make use of the time by putting into practice a method of determining the specific gravity of soluble salts which I have long intended to try.

The specific gravity of an insoluble substance is determined by the amount of distilled water which a known weight of it displaces. In the case of soluble salts it has been the custom to replace the water by a hydrocarbon or mineral oil. The objections to the use of this liquid are numerous, especially when the salt, the specific gravity of which it is desired to determine, is rare or costly. Moreover, to judge by the want of agreement among the values of the specific gravity of the same salt found by different chemists, there is greater uncertainty about the numerical results than there should be. One reason for this may be that the salts are not insoluble, but only sparingly soluble in the oil, and that sufficient attention has not been given to this point.

There is one liquid in which every soluble salt is quite insoluble, and that is its own mother-liquor at the temperature at which the one parted from the other. By immersing the salt in its own mother-liquor at the temperature of what we

* Read at the meeting of the Chemical Society of London on 6th April, 1905.

may call its birth, and by making the maintenance of this temperature a *conditio sine quâ non* of every manipulation during which the two are brought together again, errors due to uncertain solubility are eliminated, and contamination of valuable preparations is avoided. It is therefore by the immersion of each salt in its own mother-liquor that I determine its displacement; and this, combined with the weight of the salt and the specific gravity of the mother-liquor, gives the specific gravity of the salt.

It is obvious that the method is applicable only to salts which *have* a mother-liquor, such as KCl; RbBr; $CaCl_2$,-$6H_2O$; $BaCl_2 2H_2O$; it is inapplicable to salts such as $CaCl_2$; $BaCl_2$; and the like, which have no legitimate mother-liquor.

The anticyclonic meteorological conditions which prevailed during the greater part of July and August 1904 were very favorable to this class of work. The anticyclone began to give way when the work was nearly finished, and it was evident that, in the absence of artificial arrangements for the preservation of a constant laboratory temperature, this class of work cannot be carried on easily or satisfactorily except in the hottest summer weather.

It is an essential condition of success that the work be carried on in a room, for the time being, especially devoted to the purpose, and occupied by one investigator. He must have in it everything that he requires, including his balance. The window of the room must face the north, and the precautions generally to be observed are similar to those prescribed by Bunsen for the practice of his gasometric method.

The salts used in this research were the chlorides, bromides and iodides of potassium, rubidium and cæsium. The rubidium and cæsium preparations were from the works of Schuchardt in Goerlitz and were of the highest degree of purity. The potassium salts were also unexceptionable as regards quality and were supplied by Merck. All of these salts dissolve easily, and most of them abundantly, in water. They also crystallize with great readiness.

The first operation is to prepare a hot solution of the salt such that, after standing over night, or for such length of time as may be deemed sufficient, it shall furnish about 60^{cc} of mother-liquor and about 15^{cc} of crystals. In the case of the potassium salts there was no difficulty, as their solubility at all temperatures is well known. The solubility of the rubidium and cæsium salts had to be determined, at least approximately, in each case, in order to economize the costly material. The following simple method furnished the required information easily and expeditiously. A suitable vessel, beaker or flask, is weighed empty, and then with 25 grams of distilled

water, of the temperature of the air. The salt is then gradually added and the mixture stirred with the thermometer. In the case of every one of these salts the temperature falls rapidly and by as much as from 15° to 20°. The salt is added as rapidly as it is taken up by the water. When the fall of temperature slackens, a minimum is soon reached, while some salt still remains undissolved at the bottom of the vessel. It is then continually stirred; the temperature rises slowly while the salt gradually passes into solution, until, at a certain temperature the amount of salt remaining undissolved is such that a further rise of one degree of temperature will evidently cause it to disappear. The vessel is now weighed and, as result, we have the weight of salt dissolved in 25 grams of water at about the last observed temperature. With a little care it is easy to arrange that this temperature shall be in the neighborhood of that of the air. The vessel with its contents is now heated, and salt added by degrees, while the temperature rises and finally reaches the boiling point or whatever other temperature may have been determined on. Salt is added until the liquid is saturated at this temperature. The vessel is again weighed and the salt dissolved at the higher temperature is ascertained. These simple experiments, which are completed in very few minutes, furnish all the information that is required for the economical employment of the material. In the absence of more detailed information the following results obtained in the above way are worth quoting:

100 Grams of Water Dissolve

Grams	98	164	264	225	51	157	93	121	156	222
of	RbBr	RbI	RbI	CsCl	CsI	CsI	CsBr	CsBr	CsBr	CsBr
at °C	12	20	boiling	25	12	107	7·5	24·5	50	93·5

With this information there is no difficulty in preparing the solution which shall, after allowing for unavoidable loss in preparation, give the required amount of mother-liquor and of crystals. The water is warmed and the pure salt is added while the temperature is raised to that of ebullition, or to any lower temperature that may have been selected. When the salt has all passed into solution, the liquid is poured into a flat crystallizing dish and crystallization begins immediately. The area of the dish should be such that the layer of solution shall not be more than half a centimeter thick. The mother-liquor is then everywhere in close touch with the crystals. The dish is then put away in a cupboard for the night.

In the morning, the temperature of the contents of the crystallizing dish and that of the air were taken very carefully. The mother-liquor was then poured off clear into a stoppered

bottle, while the crystals were collected, allowed to drain, and dried in the ordinary way. The temperature which the mixture had when separated is noted as that at which the crystals and the mother-liquor were in equilibrium; and it is exactly at this temperature that they have to be brought together again in order to determine the specific gravity of the salt. It is at this temperature also that the specific gravity bottle is weighed when filled with distilled water and with mother-liquor respectively. In fact the temperature of equilibrium and of separation is the only temperature used.

In Table I, the experimental details are given in full in the case of one salt, namely, cæsium chloride. For the other salts the results only are given, and they are collected in Table II.

All the weights given in this paper represent the weight *in vacuo*.

The specific gravity bottle which was used was one of the common and convenient form which has a thermometer for a stopper and a lateral capillary tube for the adjustment of level. Its nominal capacity was fifty cubic centimeters. On three occasions one of 25^{cc} capacity was used for determining the displacement of the mother-liquor.

The concentration (m) of the mother-liquor is determined by titration with tenth-normal silver nitrate solution. This solution was made with the greatest care and contained exactly 17 grams of silver nitrate in one liter, at the ordinary temperature of the laboratory at the time. The burette used was divided into tenths of a cubic centimeter and had a capacity of 50^{cc}. The determination of the halogen was not made until the specific gravity had been determined, and, if the concentration was not already known within narrow limits, a preliminary titration was made, after which the volume of mother-liquor was weighed, which would certainly require 40$\pm$1^{cc} for titration. The capacity of the burette from 0 to 40^{cc} was determined by weight with great care. The concentration is stated in gram-molecules salt per 1000 grams of water.

For weighing out the salt and passing it directly into the specific gravity bottle a special and convenient form of weighing tube was used. It was made out of a stoppered specimen tube with an internal diameter of 2 centimeters and a length of 7 or 8 centimeters. The lower end of this tube was opened and a piece of thin glass tube joined to it before the blowpipe. This tube, which had a length of about 3 centimeters, had an external diameter such that it could just pass freely through the neck of the specific gravity bottle. The wide end was closed with a glass stopper and the narrow end with a small india rubber cork.

It was the custom to work so as to have about 15^{cc} of dry

TABLE I.—*Experimental Details in the Case of Cæsium Chloride.*

Formula and molecular weight of salt	MR	CsCl=168·5
Temperature	T	23·1° C.
MOTHER-LIQUOR.		
Determination of Specific Gravity.		
Weight of specific gravity bottle	w_1	38·8900 gms.
Weight of specific gravity bottle filled with distilled water	w_2	89·2399
Weight of water which fills it w_2-w_1	w_3	50·3499
Weight of sp. gr. bottle + mother-liquor	w_4	135·0620
Weight of mother-liquor w_4-w_1	w_5	96·1720
Specific gravity of mother-liquor $\frac{w_5}{w_3}$	S	1·9104
Analysis.		
Weight of mother-liquor taken	w_6	1·0334 gms.
Cb. cents. $\frac{1}{10}$ $AgNO_3$ solution used	w_7	41·21 cc.
Weight of salt equivalent to silver used $\frac{w_7 \times MR}{10000}$	w_8	0·6944 gms.
Weight of water in W gms. mother-liquor w_6-w_8	w_9	0·3390
Concentration of mother-liquor expressed in gm. molecules salt per thousand gms. water 0·1 $\frac{w_7}{w_9}$	m	12·1563
SALT IN CRYSTAL.		
Determination of Specific Gravity.		
A. Weight of first portion of salt	w_{10}	22·1229 gms.
Weight of sp. gr. bot. + salt + mother-liquor	w_{11}	146·5514
Weight of mother-liquor $w_{11}-(w_1+w_{10})$	w_{12}	85·5385
Weight of water displaced by mother-liquor $\frac{w_{12}}{s}$	w_{13}	44·7828
Weight of water displaced by salt w_3-w_{13}	w_{14}	5·5671
Specific gravity of salt $\frac{w_{10}}{w_{14}}$	D_1	3·9739
B. Weight of second portion of salt	w_{15}	26·6220 gms.
Sum of weights of the two portions $w_{10}+w_{15}$	w_{16}	48·7449
Weight of sp. gr. bottle + salt + mother-liquor	w_{17}	160·4249
Weight of mother-liquor $w_{17}-(w_1+w_{16})$	w_{18}	72·7900
Weight of water displaced by the mother-liquor $\frac{w_{18}}{s}$	w_{19}	38·1085
Weight of water displaced by the salt $w_3 . w_{19}$	w_{20}	12·2414
Specific gravity of salt $\frac{w_{16}}{w_{20}}$	D_2	3·9820
C. Weight of water displaced by salt $w_{20}-w_{14}$	w_{21}	6·6743 gms.
Specific gravity of salt $\frac{w_{15}}{w_{21}}$	D_3	3·9890
Accepted specific gravity of salt	D	3·982

salt to be added in two charges to the specific gravity bottle. These charges were intended to be nearly, though not quite, equal. The available supply was distributed between two weighing tubes by approximate weight, after which the exact weight of each portion was determined in the usual way. The two portions of cæsium chloride weighed respectively 22·1229 and 26·6220 grams, so that in the first determination of specific gravity 22·1229 grams and in the second 48·7449 grams were concerned. It is not immaterial whether the first portion is charged into the empty specific gravity bottle and the mother-liquor poured over the dry powder, or is charged into the bottle which is already about half full of mother-liquor. In the former case the elimination of the entangled air is difficult and takes time, during which it is not easy to prevent the temperature getting out of hand. By the latter process very little air is carried past the surface of the liquid and very little stirring with the thermometer, which is required on other grounds, suffices to eliminate it.

Owing to the readiness with which these salts crystallize and to the slowness with which all salts dissolve in an almost saturated solution, the temperature of the mixture of salt and mother-liquor, during the adjustment of level in the specific gravity bottle, must on no account be permitted to fall below T by even 0·01°, nor should it be allowed to rise above it by more than 0·1°. The regulation of temperature was effected entirely with a standard thermometer divided into tenths of a degree, each tenth occupying a length of rather more than one millimeter on the stem. The thermometer which forms part of the specific gravity bottle is used chiefly as a stopper of convenient form. So soon as the level of the liquid has been adjusted in the bottle, it is weighed. The temperature and pressure of the air are kept account of for the reduction of all weights to the vacuum.

When the first weighing has been completed, about 20 or 25^{cc} of the clear mother-liquor are drawn off and the second charge of dry salt is added and mixed, after which the level is adjusted, and the weight determined. In the absence of experience it might be thought that it would be difficult to draw off so much of the liquid without some of the solid salt; but no matter how much they may be stirred up, these crystallized salts settle at once and completely to the bottom when immersed in their saturated solutions, and the operation presents no difficulty. It was at first intended to make a series of three determinations with each salt, but two were found to be sufficient. During all these manipulations the temperature of the air in the laboratory never differed from that of crystallization (T=23·1°) by more than one or two tenths of a degree,

and it is only in such conditions that operations of this kind can be carried out successfully.

Before bringing the crystals together with the mother-liquor in the specific gravity bottle, the operator must realize that their common temperature when mixed is to be as nearly as possible exactly that of crystallization or equilibrium (T); and he must take such measures as his experience dictates to arrive at this end. Preliminary experiments on a somewhat extensive scale are absolutely necessary, and the success of an operation depends almost entirely on the operator and the trouble that he is prepared to take.

Table II gives for each salt, MR, the temperature, T, of equilibrium between crystals and mother-liquor, and, in condensed form, the experimental *data* of the determination of S, the specific gravity at T of the mother-liquor, that of water at the same temperature being unity; of m, the concentration of the mother-liquor in gram molecules salt per 1000 grams water, and of D_1, D_2, D_3, the three observed values, as well as D, the finally accepted value, of the specific gravity of the salt, all at T and referred to that of water at the same temperature as unity.

The letters and suffixes have the same significance as in Table I.

The figures in line T show how uniform the temperature was during the period over which the experiments were spread. All the experiments were made between the 12th and 22d of July, 1904, with the exception of those on cæsium bromide, which were made on August 10th. By that time the anticyclone had begun to break and the value of T for this salt is 21·4°. For all the other salts, T lies between 22·8° and 24·3°.

During the whole of the period the barometer was very steady, varying between 758 and 761 millimeters, and the relative humidity of the air varied between 40 and 50 per cent.

Of the three values D_1, D_2, D_3 for the specific gravity of the salt, D_1 is obtained directly from the first portion of the salt, D_2 from the sum of the two portions, and D_3 is derived from D_1 and D_2 by subtraction.

D_3 represents very nearly the mean of D_1 and D_2 and is the accepted value for the majority of the salts. It is expressed to three places of decimals, of which units in the second place are exact.

It will be noticed that in the case of rubidium chloride the value of D_1 is accepted. The second determination depends on the approximate weight of the second portion of salt when the tube was being filled, the exact weighing on the balance of precision having been accidentally omitted. The operation was however completed, and the calculation made with the approximate

TABLE II.

EXPERIMENTAL RESULTS REGARDING EACH SALT IN THE ENNEAD.

Salt: Formula / MR	KCl.	KBr.	KI.	RbCl.	RbBr.	RbI.	CsCl.	CsBr.	CsI.
Salt: Mol. weight	74·6	119·1	166·1	121·0	165·5	212·5	168·5	213·0	260·0
Temperature, T	23·4°	23·4°	24·3°	22·9°	23·0°	24·3°	23·1°	21·4°	22·8°
Specific Gravity.	MOTHER-LIQUOR.								
Weight taken, grms. w_3	59·4068	34·3044	85·9636	74·7356	81·3282	46·2696	96·1720	42·3756	78·0087
Displacement, gms. w_8	50·3524	24·9554	49·9140	49·9188	49·9196	24·9478	50·3499	24·9744	50·3658
Specific gravity, $\frac{w_3}{w_8}$ S	1·1798	1·3746	1·7222	1·4971	1·6292	1·8548	1·9101	1 6968	1·5488
Concentration.									
Gm.-mols. p. 1000 gm. H_2O, M	4·7619	5·7250	8·9344	7·7670	6·7229	8·2307	12·1563	5·3057	3·5454
Specific Gravity.	SALT IN CRYSTAL.								
A. Weight of salt, gms. w_{10}	13·3684	36·7928	27·1751	19·0112	27·0906	26·4777	22·1229	27·8926	26·3890
Displacement, gms. w_{14}	7·3271	13·7498	8·9703	7·0256	8·4700	7·7248	5·5671	6·2453	5·8545
Specific gravity, $\frac{w_{10}}{w_{14}} = D_1$	1·8245	2·676	3·0295	2·706	3·198	3·428	3·974	4·466	4·5075
B. Weight of salt, gms. w_{12}	27·4258	52·5142	52·1768	43·7750	51·5438	50·6025	48·7449	57·5390	53·3916
Displacement, gms. w_{20}	14·5322	19·6005	17·1465	15·9627	16·0568	14·7658	12·2414	12·9466	11·8423
Specific gravity, $\frac{w_{16}}{w_{20}} = D_2$	1·887	2·679	3·043	(2·74)	3·210	3·428	3·982	4·455	4·5085
C. Weight of salt, gms. w_{15}	14·0574	15·7214	25·0017	(24·76)	24·4532	24·1248	26·6220	29·6464	27·0026
Displacement, gms $w_{20}—w_{14}=w_{21}$	7·2051	5·8501	8·1762	8·9371	7·5868	7·0410	6·6743	6·7013	5·9878
Sp. gravity, $\frac{w_{15}}{w_{21}}$ D_3	1·951	2·688	3·058	(2·77)	3·223	3·426	3·989	4·424	4·509
Accepted sp. gravity, D	1·951	2·679	3·043	2·706	3·210	3·428	3·982	4·455	4·508

weight was used as a control. The result shows that the value of D_1 may be safely accepted. In case of potassium chloride the value of D_2 (1·951) is accepted, and the reason for this is as follows: The first portion of salt was in very coarse powder, and in mixing it with the mother-liquor numerous crystalline particles were observed which contained gaseous enclosures, easily perceptible by the naked eye. As was expected, the observed specific gravity proved to be low. The second portion was much more finely powdered and the specific gravity resulting from the two was higher (1·8872). But this result is affected to the full extent by the gaseous enclosures in the first portion. We therefore calculate the specific gravity from the second portion alone, which gives 1·9510 for the specific gravity.

Discussion.—It is an advantage of the method just described that it furnishes more than the mere determination of the specific gravity of the salt. Thus, by ascertaining almost simultaneously the specific gravity of the mother-liquor and the displacement in it of the crystals, both being at the temperature of equilibrium, *data* are obtained for the determination of the relation between the displacement of the salt in crystal and its apparent displacement in saturated solution at that temperature. It has not hitherto been permissible to make exact comparisons of this kind owing to the independence of the observations on the salt and on the solution, which have been available.

In discussing the results of observation it is convenient to arrange them in a more articulate form than that of Table II so as to bring each feature forward prominently and by itself.

The group of salts which forms the subject of these experiments is one of the most remarkable in nature. The salts are nine in number and include all the possible binary combinations of the members of the electro-positive triad K, Rb, Cs with those of the electro-negative triad Cl, Br, I. The two triads of simple bodies make three triads, or one *ennead* (*) of binary compounds. The relations of the different members of the ennead are best shown in a table of the form of Table III. In it the salts of the same metal, M, are all in one column, and those of the same metalloid, R, all in one line. The symbol MR represents both the formula and the molecular weight of the salt.

TABLE III.

Values of MR.

	K	Rb	Cs	
(*a*)		Formula		
	KCl	RbCl	CsCl	Cl
	KBr	RbBr	CsBr	Br
	KI	RbI	CsI	I

* From the Greek *ἐννεάς*, which signifies a body of nine.

(*b*)	Molecular weight.		
74·6	121·0	168·5	Cl
119·1	165·5	213·0	Br
166·1	212·5	260·0	I

Compartment (*a*) of Table III contains the formula and compartment (*b*) the molecular weight of each salt. The latter is the fundamental attribute of a substance, on which all its properties depend. The molecular weights of the salts which occur in one column differ by the amount of the difference of the atomic weights of the metalloids which they contain, that is, by 44·5 or 47. Similarly, contiguous salts in one line have molecular weights which differ by 46·4 or 47·5. If we consider the two diagonal triads in the ennead, we see that they are characterized by the fact that both the elements in each unit are different from those in either of the other units. Further, along the diagonal KCl–CsI the molecular weights of the units differ as much as possible from each other, while the atomic weights of the components of each unit are as nearly as possible identical, being close neighbors in the atomic series. On the other diagonal, KI–CsCl, the molecular weights of the units agree with each other as nearly as possible, while the atomic weights of the constituents of the units differ from each other as much as possible.

TABLE IV.

The Salt in Crystal.

	K	Rb	Cs	
(*a*)		Values of T (C°).		
	23·4°	22·9°	23·1°	Cl
	23·4°	23·0°	21·4°	Br
	24·3°	24·3°	22·8°	I
(*b*)		Values of D.		
	1·951	2·706	3·982	Cl
	2·679	3·210	4·455	Br
	3·043	3·428	4·508	I
(*c*)		Values of $\frac{MR}{D}$.		
	38·233	44·710	42·310	Cl
	44·460	51·553	47·820	Br
	54·580	61·986	57·670	I
(*d*)		Values of $\frac{MR}{18D}$.		
	2·124	2·489	2·350	Cl
	2·470	2·864	2·657	Br
	3·032	3·444	3·204	I

The Crystal.—Table IV contains four compartments. In the first (*a*) we have the values of T, the temperature at which the crystals and mother-liquor of each salt were in equilibrium, and that at which the various displacements were observed.

Under the experimental conditions, which have been minutely described above, it is impossible to fix in advance the exact temperature of equilibrium of the crystallizing liquid. This is given by the meteorological conditions, modified by the structural features of the laboratory and of the apartment or enclosure where crystallization takes place.

In the second compartment (*b*) we have the values of D, or the specific gravity of the salt in crystal at T, referred to that of distilled water of the same temperature as unity. The *data* in this compartment are in most cases for different, but always neighboring, temperatures. The differences of the values of T are, however, so small and those of D are so great that we may discuss the specific gravities as if they had been made at one common temperature.

On examining the values of D, we see that they increase with those of MR in Table III; but the increase is not continuous, it is remittent. It takes place *triad-wise;* and this holds whether we take the triads in column or in line. Comparing salts in the same line, we see that replacing Rb by Cs causes a rise of specific gravity which is twice as great as that caused by the substitution of Rb for K. Comparing salts in the same column, the replacement of Cl by Br causes more than double the rise caused by the substitution of I for Br. However we regard it, we see that *the specific gravity of the salts is a periodic function of their molecular weight, within the ennead.*

In the third compartment (*c*) we have the values of $\frac{MR}{D}$ or the displacement of one molecule (MR) of salt stated in grams of water, and in compartment (d) the same constant is stated in gram molecules of water $\left(\frac{MR}{18D}\right)$. In dealing with the specific gravities, we saw that, whether we follow the columns or the lines, they increase with increase of molecular weight. In the case of the molecular displacements this holds for the columns but not for the lines. In these the salts of rubidium have the greatest molecular displacement, the potassium salts have the least, and the cæsium salts occupy an intermediate position. As we shall see later, this irregularity is due to a specific peculiarity of the cæsium salts. Meantime it may be noted that the *volumetric equivalent* of one gram molecule of any of the salts of the ennead varies from 2·124 H_2O to 3·204 H_2O, the iodides having the highest and the chlorides the

lowest equivalents. The average difference between the volumetric equivalents of the iodides and bromides is 0·563 H_2O, and that between the bromides and chlorides is 0·343 H_2O.

The Mother-liquor.—The values of T are the same for the mother-liquor as for the crystals, and are presented in Table IV (*a*). In Table V (*a*) we have the values of *m* or the molecular concentration of the mother-liquor. This is expressed in gram molecules salt per 1000 grams water. It represents also with great exactness the solubility of the salt in water at T, and we shall consider it for a moment from this point of view.

TABLE V.

The Salt in Mother-liquor.

	K	Rb	Cs	
(*a*)		Values of *m*.		
	4·7619	7·7670	12·1563	Cl
	5·7250	6·7229	5·3057	Br
	8·9344	8·2307	3·5454	I
(*b*)		Values of S.		
	1·1798	1·4971	1·9101	Cl
	1·3746	1·6292	1·6968	Br
	1·7222	1·8548	1·5488	I
(*c*)		Values of $\frac{v}{m}$		
	31·223	38·069	49·021	Cl
	39·038	44·131	48·137	Br
	49·506	58·575	67·907	I
(*d*)		Values of $\frac{v}{18m}$.		
	1·735	2·115	2·723	Cl
	2·169	2·452	2·674	Br
	2·750	3·257	3·773	I

The least soluble of the nine is cæsium iodide, which has the highest molecular weight, and potassium chloride, which has the lowest molecular weight, comes next to it. Next to cæsium iodide, in molecular weight and in solubility, we have cæsium bromide; and, similarly, next to potassium chloride, in molecular weight and in solubility, we have potassium bromide. In the latter case the solubility increases with the molecular weight while in the former it decreases with it. But, if Table III be referred to, it will be observed that, as regards molecular weight, KCl and CsI occupy singular positions in the ennead. On the other hand, KBr (119·1) and RbCl (121) have almost identical molecular weights, as have also CsBr (213) and RbI (212·5), yet the solubilities in each

pair respectively are very different. The lowest solubilities are on the diagonal KCl–CsI and the highest solubilities on the diagonal KI–CsCl. RbBr, which occupies the middle place on both these diagonals, is also in the middle of the middle column and of the middle line, and is the center of the ennead. Its solubility, besides being nearly the average of the group, has a symmetrical position with respect to those of the other salts. On one diagonal the solubility of its neighbors is lower, on the other higher than its own. In its column the solubility of its neighbors is higher, in its line it is lower than its own.

In compartment (*b*) of Table V we have the values of S, the specific gravity of the mother-liquor at T, referred to that of distilled water of the same temperature as unity. These numbers cannot, as they stand, be compared with each other because they refer to solutions of such different concentrations. They enable us, however, to arrive at the average apparent displacement of one gram molecule of salt in the saturated solution which contains 1000 grams of water at T. Thus, taking again cæsium chloride as an example, we have for the weight of salt dissolved in 1000 grams of water

$$w = \text{m. CsCl} = 2048{\cdot}34 \text{ grams.}$$

Adding 1000 grams to this we have for the weight of the solution

$$W = 1000 + w = 3048{\cdot}34 \text{ grams.}$$

The specific gravity (S) being 1·9101, the displacement of the solution is

$$V = \frac{W}{S} = 1595{\cdot}92 \text{ grams of water,}$$

whence the gross apparent displacement of the salt in solution is

$$v = V - 1000 = 595{\cdot}92 \text{ grams,}$$

and the mean apparent displacement per molecule is

$$\frac{v}{m} = 49{\cdot}021 \text{ grams.}$$

In compartment (*c*) we have the value of $\frac{v}{m}$ for each member of the ennead. This expresses, in grams of water, the average apparent displacement of one gram molecule of salt in its saturated solution at T. In compartment (*d*) the same constant is expressed in terms of gram molecules of water $\left(\frac{v}{18m}\right)$.

Before commenting on the numbers in the table, it is important to form a clear conception of their physical meaning.

We shall best arrive at this by returning to our detailed example of chloride of cæsium. As the quantity of saturated solution which contains 1000 grams of water weighs 3048·34 grams and displaces 1595·92 grams of water, we may imagine it to have been prepared in the following way:—1595·92 grams of water are taken and cæsium chloride is dissolved in it so that each portion, as it is added, forms a saturated solution with the exact quantity of water which it requires for this purpose and the remainder of the water remains uncontaminated. Parallel with the dissolution of the salt, pure water is removed at such a rate as to keep the displacement or bulk of the liquid always the same. When no more salt will dissolve we have a saturated solution which contains 1000 grams of water. The weight of cæsium chloride which has entered the solution is 2048·34 grams and the weight of water which has left it is 595·92 grams, whilst the displacement of the liquid is the same at the end of the operation as it was at the beginning. In thus describing the preparation of the saturated solution, we have described an operation of substitution. *It is therefore permissible to regard solutions as products of substitution.* If we give to the above numbers their molecular interpretation, we see that the mean apparent displacement of one molecule of cæsium chloride in its saturated solution at 23·1° is equal to that of 2·723 gram molecules of water, and therefore, that, in these conditions, *CsCl is volumetrically equivalent to 2·723 H_2O.*

If we study Table V (*d*), we see that the average molecular displacement of the salts increases with their molecular weight, whether we follow the columns or the lines. The only exception is furnished by cæsium bromide, the displacement of which is very slightly lower than that of cæsium chloride. The greatest molecular displacement is that of cæsium iodide, which has the highest molecular weight; and the least molecular displacement is that of potassium chloride, which has the lowest molecular weight. The pair, potassium bromide and rubidium chloride, which have almost equal molecular weights, have also almost equal molecular displacements. The same is true of the pair, potassium iodide and cæsium chloride, but rubidium bromide has a markedly lower displacement. Finally, the pair, rubidium iodide and cæsium bromide, which have almost identical molecular weights, present no resemblance in their apparent molecular displacements.

Comparison of the Displacement of the Salt in Crystal and in Mother-liquor.—The molecular displacement $\frac{MR}{D}$ of the salts in crystal is given in Table IV (*c*) in terms of grams of water; that of the salts in mother-liquor is similarly given in Table V (*c*).

If we compare these two tables, we find the remarkable result that while in the case of the potassium and the rubidium salts the figures for the displacement in crystal are greater than those for the displacement in mother-liquor, in the case of the cæsium salts the reverse is the case.

TABLE VI.

The Salt in Crystal and in Mother-liquor.

	K	Rb	Cs	
(*a*)		Values of $\frac{MR}{D} - \frac{v}{m}$.		
	7·010	6·641	**− 6·711**	Cl
	5·422	7·422	**− 0·317**	Br
	5·074	3·411	**−10·237**	I
(*b*)		Values of $\frac{MR}{D} \cdot \frac{m}{v}$.		
	1·225	1·175	0·863	Cl
	1·139	1·168	0·993	Br
	1·103	1·059	0·849	I

In Table VI (*a*) we have the difference $\left(\frac{MR}{D} - \frac{v}{m}\right)$ of the molecular displacement of the salt in crystal from its mean molecular displacement in mother-liquor. In compartment (*b*) we have the ratio $\left(\frac{MR}{D} \cdot \frac{m}{v}\right)$ of these quantities.

Taking the figures in compartment (*a*) we see that in the case of the salts of potassium and rubidium crystallization is accompanied by considerable expansion, and this is what is usually met with. In the case of the cæsium salts the reverse is the case, and very decidedly so in the case of the chloride and of the iodide, much less so in the case of the bromide, which, in this, as in other particulars, maintains its singular position.

In this connection it should be noted that among the ratios $\left(\frac{MR}{D} \cdot \frac{m}{v}\right)$ given in compartment (*b*), the two which are nearest to unity are those for RbI (1·059) and for CsBr (0·993) respectively; and their molcular weights are almost identical. Further the salts situated *co-diagonally* to them, namely RbBr and CsI, have ratios whose difference from unity are almost equal, namely +0·168 for RbBr and −0·151 for CsI.

Taking a general view of the figures in (*b*) which give the ratios of displacement in crystal and in mother-liquor, we see great differences. The most striking examples are, as in the case of solubility, the extreme members of the ennead KCl

and CsI. The former expands by more than 25 per cent, and the latter contracts by 15 per cent on crystallizing.

These figures accentuate the peculiarity of the cæsium salts, that crystallization is accompanied by contraction. An interesting conclusion can be drawn from the behavior of the different salts in this respect, namely, that *the crystallization of the potassium and rubidium salts of the ennead must be hindered by increased pressure, while that of the cæsium salts must be helped by the same agency.*

Conclusion.—The method of determining the specific gravity of a soluble salt in its own mother-liquor, as described in the first part of the paper, involves manipulations of too delicate a character to permit it to pass into general practice in competition with other methods for the same primary purpose. When, however, the specific gravity of the salt has been ascertained in this way, the relation between its apparent displacement in the state of crystal and in that of saturated solution have been ascertained at the same time. In the second part of the paper the observations are discussed from this point of view, but owing to exigencies of space the discussion has been limited to the accentuation of the salient features. One of the most important of these is the connection which reveals itself between the molecular weight of the salts and their specific gravity and displacement in crystal and in saturated solution, in definite conditions. The authority of the periodic law makes itself as clearly felt in the limited area of the ennead as it does in the realm of the elements. It is true that the cæsium salts introduce some irregularity into the periodicity, but this is not to be looked on as an exception, but as an interference, the nature of which it will be interesting to trace.

ART. III.—*Further Work on the Interaction of Hydrochloric Acid and Potassium Permanganate in the Presence of Various Inorganic Salts;* by JAMES BROWN.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—cxliii.]

IN a previous paper* I have shown that the effect attributed by Wagner† to the catalytic action of ferric chloride in the reaction between hydrochloric acid and potassium permanganate is in reality due to oxidation of oxalic acid, added to reduce the residual oxides of manganese, by the chlorine formed during the reaction. Wagner's results of a similar nature with the chlorides of chromium, cadmium, gold, and platinum, from which he argues that these salts also act catalytically in the reaction under consideration, have recently been investigated, and it has been found that with the chlorides of gold and cadmium the assumed catalytic effect is due entirely to the chlorine retained in solution, while with the chlorides of platinum and chromium the observed differences are largely due to the chlorine retained in solution, but partly also to an excessive reduction of the permanganate, as will be shown.

Care was taken in this work to use pure salts, and for this purpose chromic chloride, platinic chloride, and auric chloride were especially prepared and purified. The chromic chloride was prepared by totally reducing potassium dichromate with strong hydrochloric acid, precipitating chromic hydroxide with ammonium hydroxide, filtering off and washing the precipitate until free from all soluble material. The chromic hydroxide was then dissolved in dilute hydrochloric acid and the excess of the acid removed by evaporating several times to small volume, replacing the water as it evaporated. In this way a solution was obtained showing slight excess of chlorine over that corresponding to the chromic chloride. The platinic chloride provided commercially was found to contain a considerable quantity of ferric chloride. This was removed by precipitating the platinum as the chlor-platinate with a concentrated solution of ammonium chloride and alcohol, filtering off and washing with alcohol until free from all iron. The ammonium chlor-platinate was then ignited to spongy platinum, the latter dissolved in aqua regia, the excess of nitric acid volatilized by continued heating with hydrochloric acid, and the large excess of hydrochloric acid in turn removed by evaporating to small volume several times. The commercial auric

* This Journal [4], vol. xix, 31.

† Maassanalytische Studien, Habilitahonsschrift, Leipzig, 1898.

chloride also contained iron. This was removed by heating with a strong solution of oxalic acid, filtering off the gold thus precipitated, and washing until free from iron and oxalic acid. The gold was then dissolved in aqua regia, and the excess of nitric and hydrochloric acids removed as with platinum.

Wagner* states that in experimenting with the various metallic chlorides which he regards as catalyzers, he used tenth-normal solutions of the same content in chlorine. This with chlor-platinic acid would mean a solution containing $\frac{19{\cdot}5}{6}=3{\cdot}25$ grams of platinum to the liter since chlor-platinic acid contains six atoms of chlorine to the molecule. With chlor-auric acid it means $\frac{19{\cdot}73}{4}=4{\cdot}9322$ grams of gold to the liter since chlor-auric acid contains four atoms of chlorine to the molecule. Similarly tenth-normal solutions of chromic chloride, cadmium chloride, and ferric chloride must contain 1·7366 grams chromium, 5·6 grams cadmium, and 1·8666 grams iron, respectively. The solutions used in the experiments about to be described were standardized in this way in respect both to chlorine and metal, and in no case showed a noticeable excess of chlorine, the excess never exceeding the equivalent of one or two hundredths of a cubic centimeter of normal hydrochloric acid.

Experiments were then conducted in the following manner: To a 300$^{cm^3}$ flask were added 100$^{cm^3}$ of normal hydrochloric acid, and in addition either 9·90$^{cm^3}$ of tenth-normal ferric chloride, cadmium chloride, chromic chloride, chlor-platinic acid, or chlor-auric acid. Of approximately twentieth-normal potassium permanganate 9·90$^{cm^3}$ were then added, and the flask fitted in a ground joint to a return condenser approximately 60$^{cm^3}$ in length, was heated for one hour, or thirty minutes, on the Ostwald thermostat at a temperature of 50° C. Of approximately tenth-normal oxalic acid 9·90$^{cm^3}$ were then added, and permanganate run in to color. Calculations of the amount of permanganate "apparently reduced" were then made by subtracting the permanganate equivalent of the oxalic acid from the total permanganate used, (that is the "$KMnO_4$ before digestion" plus the "$KMnO_4$ to color.") Similarly the "$KMnO_4$ apparently unreduced" is obtained by subtracting the "$KMnO_4$ apparently reduced" from the "$KMnO_4$ before digestion."

* Loc. cit., p. 85.

The results follow:

TABLE I.

[20^{cm^3} $\frac{N}{20}(H_4N)_2C_2O_4 = 20{\cdot}09^{cm^3}$ $KMnO_4$. Oxygen value $KMnO_4 = 0{\cdot}0003982$ grm. per cm^3. $9{\cdot}90^{cm^3}$ $H_2C_2O_4 = 19{\cdot}62^{cm^3}$ $KMnO_4$.]

$\frac{N}{1}$HCl cm^3.	$\frac{N}{10}$HCl cm^3.	$KMnO_4$ before digestion cm^3.	Temperature C°.	Time of digestion min.	$H_2C_2O_4$ cm^3.	$KMnO_4$ to color cm^3.	$KMnO_4$ apparently reduced during digestion cm^3.	$KMnO_4$ apparently unreduced during digestion cm^3.
100	9·90	9·90	50	60	9·90	12·28	2·56	7·34
100	9·90	9·90	50	60	9·90	12·11	2·39	7·51
100	9·90	9·90	50	60	9·90	12·53	2·81	7·09
100	9·90	9·90	50	60	9·90	12·69	2·97	6·93
100	9·90	9·90	50	60	9·90	12·61	2·89	7·01
100	9·90	9·90	50	60	9·90	12·51	2·79	7·11
100	9·90	9·90	50	60	9·90	12·70	2·98	6·92
	$\frac{N}{10}CdCl_2$ cm^3.							
100	9·90	9·90	50	60	9·90	13·35	3·63	6·27
100	9·90	9·90	50	60	9·90	13·20	3·48	6·42
100	9·90	9·90	50	60	9·90	13·23	3·51	6·39
100	9·90	9·90	50	60	9·90	13·75	4·03	5·87
100	9·90	9·90	50	60	9·90	13·79	4·07	5·83
	$\frac{N}{10}CrCl_3$ cm^3.							
100	9·90	9·90	50	60	9·90	12·88	3·16	6·74
100	9·90	9·90	50	60	9·90	12·84	3·12	6·78
100	9·90	9·90	50	60	9·90	12·71	2·99	6·91
100	9·90	9·90	50	60	9·90	13·18	3·46	6·44
100	9·90	9·90	50	60	9·90	13·28	3·56	6·34
	$\frac{N}{10}\frac{H_2PtCl_6}{6}$ cm^3.							
100	9·90	9·90	50	60	9·90	14·77	5·05	4·85
100	9·90	9·90	50	60	9·90	14·13	4·41	5·49
100	9·90	9·90	50	60	9·90	13·95	4·23	5·67
100	9·90	9·90	50	60	9·90	14·35	4·63	5·27
100	9·90	9·90	50	60	9·90	13·77	4·05	5·85

TABLE I (continued).

[$20^{cm^3}\ \frac{N}{20}\ (H_4N)_2C_2O_4 = 20{\cdot}09^{cm^3}\ KMnO_4$. Oxygen valve $KMnO_4 = 0{\cdot}0003982$ grm. per cm^3. $9{\cdot}90^{cm^3}\ H_2C_2O_4 = 19{\cdot}62^{cm^3}\ KMnO_4$.]

$\frac{N}{1}$HCl cm^3.	$\frac{N}{10}\frac{HAuCl_4}{4}$ cm^3.	$KMnO_4$ before digestion cm^3.	Temperature C°.	Time of digestion min.	$H_2C_2O_4$ cm^3.	$KMnO_4$ to color cm^3.	$KMnO_4$ apparently reduced during digestion cm^3.	$KMnO_4$ apparently unreduced during digestion cm^3.
100	9·90	9·90	50	60	9·90	13·97	4·25	5·65
100	9·90	9·90	50	60	9·90	13·73	4·01	5·89
100	9·90	9·90	50	60	9·90	13·35	3·63	6·27
100	9 90	9·90	50	60	9·90	14·27	4·55	5·35
100	9·90	9·90	50	60	9·90	13·02	3·30	6·60
	$\frac{N}{10}FeCl_3$ cm^3.							
100	9·90	9·90	50	60	9·90	13·46	3·74	6·16
100	9·90	9·90	50	60	9·90	14·45	4·73	5·17
100	9·90	9·90	50	60	9·90	13·72	4·00	5·90
100	9·90	9·90	50	60	9·90	14·01	4·29	5·61
100	9·90	9·90	50	60	9·90	13·92	4·20	5·70

From these results it may be seen that in accordance with Wagner's views, there is more permanganate required to bring about final coloration in those experiments in which the various chlorides which he regards as catalyzers are used than in their absence. To ascertain whether these differences are due to the interfering action of the chlorine as shown with ferric chloride in the previous paper,* the experiments of Table II were performed in a manner identical with those of Table I, except that a current of air dried and purified was passed through the liquid while digesting to remove the chlorine.

The results of these experiments are outlined in Table II.

TABLE II.

[$KMnO_4$ and $H_2C_2O_4$ solutions same as used in Table I.]

$\frac{N}{1}$HCl cm^3.	$\frac{N}{10}$HCl cm^3.	$KMnO_4$ before digestion cm^3.	Temperature C°.	Time of digestion min.	$H_2C_2O_4$ cm^3.	$KMnO_4$ to color cm^3.	$KMnO_4$ apparently reduced during digestion cm^3.	$KMnO_4$ apparently unreduced during digestion cm^3.
100	9·90	9·90	50	60	9·90	18·14	8·42	8·48
100	9·90	9·90	50	60	9·90	18·12	8·40	8·50
100	9·90	9·90	50	60	9·90	18·08	8·36	8·54
100	9·90	9·90	50	60	9·90	18·09	8·37	8·53
100	9·90	9·90	50	60	9·90	18·10	8·38	8·52

* Loc. cit., p. 36.

TABLE II (continued).

[$KMnO_4$ and $H_2C_2O_4$ solutions same as used in Table I.]

$\frac{N}{1}HCl$ cm³.	$\frac{N}{10}CdCl_2$ cm³	$KMnO_4$ before digestion cm³.	Temperature C°.	Time of digestion min.	$H_2C_2O_4$ cm³.	$KMnO_4$ to color cm³.	$KMnO_4$ apparently reduced during digestion cm³.	$KMnO_4$ apparently unreduced during digestion cm³.
100	9·90	9·90	50	60	9·90	18·11	8·39	8·51
100	9·90	9·90	50	60	9·90	18·09	8·37	8·53
100	9·90	9·90	50	60	9·90	18·13	8·41	8·49
100	9·90	9·90	50	60	9·90	18·08	8·36	8·54
100	9·90	9·90	50	60	9·90	18·05	8·33	8·57
	$\frac{N}{10}CrCl_3$ cm³							
100	9·90	9·90	50	60	9·90	16·72	7·00	2·90
100	9·90	9·90	50	60	9·90	16·99	7·27	2·63
100	9·90	9·90	50	60	9·90	17·01	7·29	2·61
100	9·90	9·90	50	60	9·90	16·76	7·04	2·86
100	9·90	9·90	50	60	9·90	16·71	6·99	2·91
	$\frac{N}{10}\frac{H_2PtCl_6}{6}$ cm³							
100	9·90	9·90	50	60	9·90	19·62	9.90	0·00
100	9·90	9·90	50	60	9·90	19·67	9·90	0·00
100	9·90	9·90	50	60	9·90	19·69	9·90	0·00
100	9·90	9·90	50	60	9·90	19·65	9·90	0·00
100	9·90	9·90	50	60	9·90	19·51	8·79	0·11
100	9·90	9·90	50	60	9·90	19·51	8·79	0·11
	$\frac{N}{10}\frac{HAuCl_4}{4}$ cm³							
100	9·90	9·90	50	60	9·90	18·12	8·40	1·50
100	9·90	9·90	50	60	9·90	18·07	8·35	1·55
100	9·90	9·90	50	60	9·90	18·14	8·42	1·48
100	9·90	9·90	50	60	9·90	18·09	8·37	1·53
100	9·90	9·90	50	60	9·90	18·15	8·43	1·47
	$\frac{N}{10}FeCl_3$ cm³							
100	9·90	9·90	50	60	9·90	18·14	8·42	1·48
100	9·90	9·90	50	60	9·90	18·05	8·33	1·57
100	9·90	9·90	50	60	9·90	18·07	8·35	1·55
100	9·90	9·90	50	60	9·90	18·09	8·37	1·53
100	9·90	9·90	50	60	9·90	18·15	8·43	1·47

Here it is shown, as with ferric chloride in the previous paper, that the chlorine held in solution is responsible for the low indications of the amount of permanganate apparently reduced during digestion when no means are used to remove this chlorine. With cadmium chloride and chlor-auric acid the same amount of permanganate is here shown to be reduced as when the permanganate is digested with hydrochloric acid alone, and it is further seen that the maximum effect is accomplished by thirty minutes heating. In all experiments in which chlor-platinic acid was used the oxides of manganese, noticeable in those experiments in which ferric, cadmic, and chromic chlorides were used, were entirely reduced, and the liquid at the close of the digestion was perfectly clear, showing only the color due to the chlor-platinic acid; when the chlorine is removed in these experiments the permanganate required to bring about final coloration is substantially equal to the oxalic acid added, the slight excess over this value being due probably to difficulty of distinguishing the end color. In the last two experiments the values are a little below that corresponding to the oxalic acid; this may be due to a slight residue of manganese oxides which appeared not to be entirely reduced at the end of the half hour's digestion. This point, however, has not been sufficiently investigated to be definitely decided. With chromic chloride we find a variety of phenomena. In all experiments shown in Tables I and II the permanganate is entirely reduced and the chromic chloride is partially oxidized, leaving at the end of the digestion a clear liquid greenish-yellow in color. When the oxalic acid is added the chromic acid is reduced totally or in part, tending to restore the original green color to the solution, but the chromic chloride does not seem to be oxidized to any noticeable extent on running in permanganate to color, the end reaction showing a green liquid colored faintly by the permanganate. In an experiment showing such a variety of reactions, most of which are indefinite, concordance of results is not to be expected even when the chlorine is removed, and the experiments of Tables I and II, in which chromic chloride were used, show wide variation.

Wagner* has noted the separation of hydrated oxides of manganese with all his "catalyzers" except gold and platinum. The exception holds for platinum but not for gold, in my experience, as with the latter the same residual oxides of manganese are noticeable as with ferric and cadmic chlorides. With chromic chloride I found no residual oxides, as already stated, Wagner's statement to the contrary notwithstanding.

It will be seen by a comparison of the results of Table I of this paper with those of Table I of the previous paper, that although in both tables the "$KMnO_4$ apparently reduced during digestion" is greater in the presence of the metallic chlor-

* Loc. cit., page 87.

ides than in their absence, the readings of the present paper are considerably greater than corresponding readings in the previous paper. These differences can be explained on the evident supposition that the oxidation of the oxalic acid by the chlorine was more extensive in the experiments recorded in this paper than in those of Table I of the previous paper, for these differences disappear when the chlorine is removed from the sphere of action, the differences between the readings of Tables II and III of the previous paper on the one hand and those of Table II of the present paper on the other being small and in all probability due to differences in the strength of the permanganate solution used. The experiments of this paper were made with as little shaking as possible to avoid expulsion of chlorine mechanically, and allow the chlorine to exert its maximum oxidizing effect on the oxalic acid during the time of the titration. These variations show still more conclusively the non-concordance likely in Wagner's process, and the dependence of results on the oxidizing action of the chlorine.

The conclusion must be drawn, then, that Wagner's results with each of the salts which he regards as catalyzers are in all cases largely dependent on the oxidizing action of the chlorine held in solution. With ferric chloride, cadmium chloride, and chlor-auric acid, the assumed catalytic effect of chlor-metal acids formed by the union of the metallic chlorides with hydrochloric acid, which are more easily oxidized by potassium permanganate than is hydrochloric acid, is unsubstantiated. With these three compounds the apparent catalytic effect is due entirely to the chlorine retained in solution. With chromic chloride and chlor-platinic acid the observed differences are due partly to the chlorine retained in solution but partly also to the total reduction of the residual oxides of manganese. With platinic chloride the action is apparently catalytic, this compound exerting a reducing action on the higher oxides of manganese formed in the presence of the other compounds. With chromic chloride the action is not catalytic, the assumed catalyzer being oxidized to chromate, thus losing its identity, as is not the case with a true catalyzer.

Another series of experiments was made to ascertain whether any difference in the amount of higher oxides of manganese formed in the presence of ferric chloride, cadmium chloride, or chlor-auric acid, or in the amount of chromate formed in the presence of chromic chloride, is caused by the removal of chlorine in the experiments of Table II. Experiments were made as were those of Table I, the digestion being continued one hour without the removal of chlorine, and the chlorine then removed by blowing a current of air through the solution for one-half hour. Oxalic acid was then added and perman-

ganate run in to color as before. The results showed all desired agreement with those of Table II, proving that the removal of chlorine during the hour's digestion has no effect on the oxidizing material other than chlorine retained. As these experiments were merely confirmatory, they are not given here.

Wagner has also shown the diminishing effect of manganous chloride* and sulphate in the amount of permanganate apparently reduced by hydrochloric acid after the above method of experimentation. This part of his work has also been investigated and gives results as shown in Table III, in which the chlorine was not removed during digestion, and Table IV, in which the chlorine was thus removed. Difficulty was encountered in maintaining the solutions of manganous salts at constant value in neutral solution, basic manganese salts settling out on standing a few days. One hundred and twenty cubic centimeters of normal hydrochloric acid to the liter were therefore added in making up the tenth-normal manganous salts. This would make an excess of approximately $1{\cdot}20^{cm^3}$ of normal hydrochloric acid in $9{\cdot}90^{cm^3}$ of the solutions, the amount used in the experiments; allowance was made for this excess, and only $98{\cdot}80^{cm^3}$ of normal hydrochloric acid used.

TABLE III.

[20^{cm^3} $\frac{N}{10}(H_4N)_2C_2O_4 = 40{\cdot}99^{cm^3}$ $KMnO_4$ Oxygen value $KMnO_4 = 0{\cdot}0003903$ grm. per cm^3. $9{\cdot}90^{cm^3}$ $H_2C_2O_4 = 20{\cdot}75^{cm^3}$ $KMnO_4$.]

$\frac{N}{1}HCl$ cm^3.	$\frac{N}{10}HCl$ cm^3.	$KMnO_4$ before digestion cm^3.	Temperature C°.	Time of digestion min.	$H_2C_2O_4$ cm^3.	$KMnO_4$ to color cm^3.	$KMnO_4$ apparently reduced during digestion cm^3.	$KMnO_4$ apparently unreduced during digestion cm^3
100	9·90	9·90	50	60	9·90	13·08	2·23	7·67
100	9·90	9·90	50	60	9·90	13·18	2·33	7·57
100	9·90	9·90	50	60	9·90	13·33	2·48	7·42
100	9·90	9·90	50	60	9·90	13·17	2·32	7·58
100	9·90	9·90	50	60	9·90	13·22	2·37	7·53
	$\frac{N}{10}MnCl_2$ cm^3							
100	9·90	9·90	50	60	9·90	12·45	1·60	8·30
100	9·90	9·90	50	60	9·90	12·38	1·53	8·37
100	9·90	9·90	50	60	9·90	12·59	1·74	8·16
100	9·90	9·90	50	60	9·90	12·35	1·50	8·40
100	9·90	9·90	50	60	9·90	12·36	1·51	8·39

* Loc. cit., p. 88.

TABLE III (continued).

[$20^{cm^3}\frac{N}{10}(H_4N)_2C_2O_4 = 40{\cdot}99^{cm^3}\ KMnO_4$. Oxygen value $KMnO_4 = 0{\cdot}0003903$ grm. per cm. $9{\cdot}90^{cm^3}\ H_4C_2O_4 = 20{\cdot}75^{cm^3}\ KMnO_4$].

$\frac{N}{1}HCl$ cm³.	$\frac{N}{10}MnSO_4$ cm³.	$KMnO_7$ before digestion cm³.	Temperature C°.	Time of digestion min.	$H_2C_2O_4$ cm³.	$KMnO_4$ to color cm³.	$KMnO_4$ apparently reduced during digestion cm³.	$KMnO_4$ apparently unreduced during digestion cm³.
100	9·90	9·90	50	60	9·90	12·48	1·63	8·27
100	9·90	9·90	50	60	9·90	12·45	1·60	8·30
100	9·90	9·90	50	60	9·90	12·51	1·66	8·24
100	9·90	9·90	50	60	9·90	12·55	1·70	8·20
100	9·90	9·90	50	60	9·90	12·25	1·40	8·50

TABLE IV.

[$KMnO_4$ and $H_2C_2O_4$ solutions same as used in Table III.]

$\frac{N}{1}HCl$ cm³.	$\frac{N}{10}HCl$ cm³.	$KMnO_4$ before digestion cm³.	Temperature C°.	Time of digestion min.	$H_2C_2O_4$ cm³.	$KMnO_4$ to color cm³.	$KMnO_4$ apparently reduced during digestion cm³.	$KMnO_4$ apparently unreduced during digestion cm³.
100	9·90	9·90	50	60	9·90	19·59	8·74	1·16
100	9·90	9·90	50	60	9·90	19·55	8·70	1·20
100	9·90	9·90	50	60	9·90	19·48	8·63	1·27
100	9·90	9·90	50	60	9·90	19·66	8·81	1·09
100	9·90	9·90	50	60	9·90	19·64	8·79	1·11
100	9·90	9·90	50	60	9·90	19·53	8·68	1·22
	$\frac{N}{10}MnCl_2$ cm³.							
100	9·90	9·90	50	60	9·90	16·61	5·76	4·14
100	9·90	9·90	50	60	9·90	17·09	6·24	3·66
100	9·90	9·90	50	60	9·90	16·38	5·53	4·37
100	9·90	9·90	50	60	9·90	16·92	6·07	3·83
100	9·90	9·90	50	60	9·90	16·68	5·83	4·07
100	9·90	9·90	50	60	9·90	16·89	6·04	3·86
	$\frac{N}{10}MnSO_4$ cm³.							
100	9·90	9·90	50	60	9·90	16·68	5·83	4·07
100	9·90	9·90	50	60	9·90	16·89	6·04	3·86
100	9·90	9·90	50	60	9·90	16·65	5·80	4·10
100	9·90	9·90	50	60	9·90	16·77	5·92	3·98
100	9·90	9·90	50	60	9·90	16·43	5·58	4·32
100	9·90	9·90	50	06	9·90	16·57	5·72	4·18

Here it is seen that, as shown by Wagner, less permanganate is required to bring about final coloration in those experiments in which manganous sulphate or chloride was used than in their absence. From the experiments recorded in Table IV, it must be concluded that this diminishing effect is due to the intervention of the Guyard reaction so that the higher oxides of manganese are formed in larger proportion by the introduction of the manganous salt, thus giving more material (if we disregard the volatile and indefinitely reacting chlorine when it is retained in solution) to oxidize the oxalic acid. Wagner has attributed this diminishing effect to a slowing of the reaction between hydrochloric acid and thinks such is the protecting influence of a manganous salt in titrations of ferrous salts by potassium permanganate in the presence of hydrochloric acid. It is a diminishing of the reaction between hydrochloric acid and potassium permanganate, but this diminishing is due to the formation of higher oxides of manganese, which, as is well known, are less easily reduced by hydrochloric acid than is the permanganate itself. Such action is unquestionably the intervention of the Guyard reaction, as first suggested by Zimmermann.*

It has been found that with each of the salts which Wagner regards as catalyzers the apparent catalytic effect is entirely or largely due to the chlorine retained in solution. The question therefore arises: In what way does the chlorine affect the result? It is evidently effective in oxidizing the oxalic acid. It seemed likely, therefore, that the lesser oxidation of the oxalic acid, necessitating a greater amount of permanganate to bring about final coloration, in the presence of the various chlorides used, is due to a lesser retention of chlorine in the presence of these salts. It was decided, therefore, to determine the chlorine retained in solution under the varying conditions, and also the residual higher oxides of manganese or with the chromic chloride the chromate formed during digestion, thus obtaining the total oxidizing value of the material retained in solution at the close of the hour's digestion. For this purpose potassium permanganate was digested with hydrochloric acid in the presence and absence of the various salts used in the preceding experiments of this paper for one hour at a temperature of 50° C. as there indicated. The flask containing the liquids was sealed to a Voit flask, to which was fitted in a ground joint a return condenser approximately 60^{cm} in length and with a bore approximately 3^{cm} in diameter. At the close of the hour's digestion this condenser was removed,

* Ann. Chem., ccxiii, 311 (1882).

and the Voit flask connected with a Drexel washing-bottle containing about 300^{cm^3} of an approximately two per cent solution of potassium iodide, the Drexel washing-bottle being joined to Will and Varrentrapp bulbs also containing a strong solution of potassium iodide to absorb escaping iodine fumes. The chlorine retained in solution in the flask was driven into the potassium iodide by means of a strong current of air dried and purified in the usual manner, the liberated iodine titrated by means of an approximately twentieth-normal solution of sodium thiosulphate, and its equivalent in permanganate calculated. In those experiments in which the digestion was made with hydrochloric acid alone, and in the presence of cadmium chloride and chromic chloride, the "oxidizing material not chlorine" was determined by adding potassium iodide to the digestion liquid after the removal of the chlorine, and titrating the liberated iodine with sodium thiosulphate. Its permanganate equivalent was then estimated as indicated in the table. By adding together the "$KMnO_4$ equivalent" of the chlorine retained in solution during digestion and the "$KMnO_4$ equivalent" of the "oxidizing material not Cl formed during digestion" we have the "total $KMnO_4$ found." The difference between this last value and the "$KMnO_4$ before digestion" gives the "$KMnO_4$ lost" as indicated in Table V. Since, however, potassium iodide could not be added to the solution containing ferric and auric chlorides because of the reduction of these salts with liberation of iodine, an action probably indefinite under the conditions of experimentation, the average of the permanganate equivalent of the "oxidizing material not Cl" obtained with hydrochloric acid alone and with cadmium chloride was taken as indicating the same value with ferric and auric chloride. The results of Table II have shown that the residual oxides of manganese are substantially constant with hydrochloric acid alone and with cadmium, ferric, and auric chlorides. So no error is introduced by the procedure here adopted. Calculations of "$KMnO_4$ found" and "$KMnO_4$ lost" were then made as with hydrochloric alone, and with cadmium chloride. The results follow:

TABLE V.

20^{cm^3} $\frac{N}{10}(H_4N)_2C_2O_4 = 40{\cdot}98^{cm^3}$ $KMnO_4$. Oxygen value $KMnO_4 = 0{\cdot}0003904$ grm. per cm^3. Iodine value, $Na_2S_2O_3 = 0{\cdot}005726$ grm. per cm^3. $9{\cdot}90^{cm^3}$ $KMnO_4 = 10{\cdot}17^{cm^3}$ $Na_2S_2O_3$. 1^{cm^3} $Na_2S_2O_3 = 0{\cdot}923^{cm^3}$ $Na_2S_2O_3$.

$\frac{N}{1}$HCl	$\frac{N}{10}$HCl	$KMnO_4$	Time Digestion min.	Temperature C°	Time to expel Cl min.	Cl retained during digestion		Oxidizing material not Cl formed during digestion		Total $KMnO_4$ found	$KMnO_4$ lost
						$Na_2S_2O_3$	$KMnO_4$ Equiv.	$Na_2S_2O_3$	$KMnO_4$ Equiv.		
cm^3	cm^3	cm^3				cm^3	cm^3	cm^3	cm^3	cm^3	cm^3
100	9·90	9·90	60	50	30	8·62	7·95	1·48	1·36	9·31	0·59
100	9·90	9·90	60	50	30	8·69	8·02	1·48	1·36	9·38	0·52
100	9·90	9·90	60	50	30	8·64	7·97	1·41	1·30	9·27	0·63
100	9·90	9·90	60	50	30	8·69	8·02	1·47	1·35	9·37	0·53
100	9·90	9·90	60	50	30	8·82	8·14	1·47	1·35	9·49	0·41
100	9·90	9 90	60	50	30	8·64	7·97	1·41	1·30	9·27	0·63
100	9 90	9·90	60	50	30	8·67	8·00	1·48	1·36	9·36	0·54
100	9·90	9·90	60	50	30	8·83	8·15	1·41	1·30	9·45	0·45
100	9·90	9·90	60	50	30	8·79	8·11	1·47	1·35	9·46	0·44
	$\frac{N}{10}CdCl_2$ cm^3										
100	9·90	9·90	60	50	30	7·66	7·07	1·42	1·31	8·38	1·52
100	9·90	9·90	60	50	30	7·68	7·08	1·40	1·29	8·37	1·53
100	9·90	9·90	60	50	30	7·64	7·05	1·39	1·28	8·33	1·57
100	9·90	9·90	60	50	30	7·69	7·09	1·45	1·33	8·42	1·48
100	9·90	9·90	60	50	30	7·65	7·06	1·39	1·28	8·34	1·56
	$\frac{N}{10}CrCl_3$ cm^3										
100	9·90	9·90	60	50	30	7·64	7·05	2·07	1·91	8·96	0·94
100	9·90	9·90	60	50	30	7·57	6·98	2·09	1·92	8·90	1·00
100	9·90	9·90	60	50	30	7·50	6·92	2·06	1·90	8·82	1·08
100	9·90	9·90	60	50	30	7·62	7·03	2·09	1·92	8·95	0·95
100	9·90	9·90	60	50	30	7·64	7·05	2·08	1·91	8·96	0·94
	$\frac{N}{10}FeCl_3$ cm^3										
100	9·90	9·90	60	50	30	8·59	7·92	....	[1·32]	9·24	0·66
100	9·90	9·90	60	50	30	8·89	8·20	....	[1·32]	9·52	0·38
100	9·90	9·90	60	50	30	8·69	8·02	....	[1·32]	9·34	0·56
100	9·90	9·90	60	50	30	8·64	7·97	....	[1·32]	9·29	0·61
100	9·90	9·90	60	50	30	8·88	8·19	....	[1·32]	9·51	0·39
	$\frac{N}{10}\frac{H_2PtCl_6}{6}$ cm^3										
100	9·90	9·90	60	50	30	10·08	9·30	....	....	9·30	0·60
100	9·90	9·90	60	50	30	10·14	9·35	....	....	9·35	0·55
100	9·90	9·90	60	50	30	10·01	9·23	....	....	9·23	0·67
100	9·90	9·90	60	50	30	10·12	9·34	....	....	9·34	0·56
100	9·90	9·90	60	50	30	10·07	9·29	....	....	9·29	0·61

TABLE V (continued).

20^{cm^3} $\frac{N}{10}(H_4N)_2C_2O_4 = 40{\cdot}98^{cm^3}$ $KMnO_4$. Oxygen value $KMnO_4 = 0{\cdot}0003904$ grm. per cm^3. Iodine value, $Na_2S_2O_3 = 0{\cdot}005726$ grm. per cm^3. $9{\cdot}90^{cm^3}$ $KMnO_4 = 10{\cdot}71^{cm^3}$ $Na_2S_2O_3$. 1^{cm^3} $Na_2S_2O_3 = 0{\cdot}924^{cm^3}$ $Na_2S_2O_3$.

$\frac{N}{1}$HCl	$\frac{N}{10}\frac{HAuCl_4}{4}$	$KMnO_4$	Time Digestion min.	Temperature C°	Time to expel Cl min.	Cl retained during digestion		Oxidizing material not Cl formed during digestion		Total $KMnO_4$ found	$KMnO_4$ lost
						$Na_2S_2O_3$	$KMnO_4$ equiv.	$Na_2S_2O_3$	$KMnO_4$ equiv.		
cm^3	cm^3	cm^3				cm^3	cm^3	cm^3	cm^3	cm^3	cm^3
100	9·90	9·90	60	50	30	8·62	7·95	....	[1·32]	9·27	0·63
100	9·90	9·90	60	50	30	8·77	8·09	....	[1·32]	9·41	0·49
100	9·90	9·90	60	50	30	8·80	8·12	....	[1·32]	9·44	0·46
100	9·90	9·90	60	50	30	8·85	8·15	....	[1·32]	9·47	0·43
100	9·90	9·90	60	50	30	8·83	8·15	....	[1·32]	9·47	0·43
	$\frac{N}{10}MnCl_2$ cm^3										
100	9·90	9·90	60	50	30	4·81	4·43	5·51	5·08	9·51	0·39
100	9·90	9·90	60	50	30	5·71	5·27	4·86	4·48	9·75	0·15
100	9·90	9·90	60	50	30	5·63	5·19	4·74	4·37	9·56	0·34
100	9·90	9·90	60	50	30	5·52	5·09	4·88	4·50	9·59	0·31
100	9·90	9·90	60	50	30	5·85	5·39	4·63	4·27	9·66	0·24
100	9·90	9·90	60	50	30	5·77	5·32	4·81	4·43	9·75	0·15
	$\frac{N}{10}MnSO_4$ cm^3										
100	9·90	9·90	60	50	30	5·72	5·27	4·79	4·42	9·69	0·21
100	9·90	9·90	60	50	30	5·66	5·22	4·83	4·45	9·67	0·23
100	9·90	9·90	60	50	30	5·42	5·00	5·09	4·69	9·69	0·21
100	9·90	9·90	60	50	30	5·78	5·33	4·73	4·36	9·69	0·21
100	9·90	9·90	60	50	30	4·23	3·90	6·36	5·87	9·77	0·13

Here it is seen that the total oxidizing material retained in solution, or the "total $KMnO_4$ found" is substantially the same with hydrochloric acid alone, and in the presence of auric and ferric chlorides. With cadmium chloride there is a considerable falling off in the chlorine retained in solution while the residual oxides of manganese show on the average only a slightly smaller value than with hydrochloric acid alone. There is, therefore, a deficiency of about $1{\cdot}00^{cm^3}$ in "total $KMnO_4$ found" as compared with the value found with hydrochloric acid alone. With platinic chloride the "total $KMnO_4$ found," or oxidizing material retained in solution, in this case all chlorine, is substantially equal to that found with hydrochloric acid alone. With chromic chloride there is a deficiency after adding together the permanganate equivalents of the chlorine retained in solution and the "oxidizing material not Cl," presumably in this case chromic acid. With manga-

nous chloride and sulphate the "$KMnO_4$ found" is slightly greater than with the hydrochloric acid alone, due probably to a lesser formation of the more volatile and indefinitely reacting product chlorine, more permanganate going to form the more definitely reacting oxides of manganese than in the digestion with hydrochloric acid alone. The amount of manganese oxides represented by "oxidizing material not Cl" in the above table is seen to vary widely. This is in accordance with Volhard's* assertion that acids hinder the reaction between manganous salts and permanganate to give higher oxides of manganese. This action, rather indefinite under even the most favorable conditions, might be expected to be especially so in the presence of the large amount of acid used in these experiments.

With all the salts above used, and especially with cadmium chloride, the "total $KMnO_4$ found" is less than the permanganate added before digestion. The natural supposition seemed to be that this deficiency was due to the escape of chlorine during the digestion. On adding potassium iodide solution, however, to the Voit flask during the hour's digestion, no appreciable escape of chlorine was noticeable, while the oxidizing material showed the same values as in Table V. This was true whether the digestion was made with hydrochloric acid alone or in the presence of any one of the salts used in Table V. It appeared evident, therefore, that the chlorine disappeared in the digestion liquid, and that the greater or less extent of this disappearance accounted for the greater or less amount of chlorine found to be present in the digestion liquid at the close of the hour's heating. Thinking that possibly these various salts might interfere in some way with the iodine liberated by permanganate from potassium iodide in the presence of hydrochloric acid, experiments were made to ascertain whether any of the observed differences were due to such interference. These experiments were conducted as follows: Into a flask were introduced 100^{cm^3} of normal hydrochloric acid, and in addition either $9{\cdot}90^{cm^3}$ of tenth-normal hydrochloric acid, or $9{\cdot}90^{cm}$ of one of the tenth-normal salt solutions there indicated. An excess of potassium iodide was then added, $9{\cdot}90^{cm^3}$ of permanganate run in and the iodine liberated estimated with sodium thiosulphate.

These experiments showed that normal values are obtained by titrating iodine by thiosulphate in the presence of hydrochloric acid and any one of the various salts used, thus excluding the possible inference that the large amount of acid or possibly the metallic chlorides interfered in the reaction.

* Ann. Chem., cxcviii, 337 (1879).

The variations above noted must therefore be due to some secondary reaction occurring during the digestion. The experiments outlined in Table VI were therefore made with varying periods of digestion, to note more carefully the progress of these variations. The manner of experimentation was to digest solutions made up as were those of Table V on the water bath during varying periods of time with the Voit flask trapped with potassium iodide solution to prevent escape of chlorine. After the digestion an excess of potassium iodide solution was added and the liberated iodine determined by use of sodium thiosulphate. In this way the total oxidizing material formed during digestion is estimated in one operation rather than in two, as was the case in the experiments of Table V. Results are indicated in Table VI.

TABLE VI.

Oxygen value, $KMnO_4$=0·0003894 grm. per cm³. Iodine value $Na_2S_2O_3$=0·005671 grm. per cm³. 9·90^{cm3} $KMnO_4$=10·80^{cm3} $Na_2S_2O_3$. 1^{cm3} $Na_2S_2O_3$=0·917^{cm3} $KMnO_4$.

$\frac{N}{1}$HCl cm³.	$\frac{N}{10}$HCl cm³.	H_2O cm³.	$KMnO_4$ cm³.	Time digestion min.	Temperature C°.	$Na_2S_2O_3$ cm³.	$KMnO_4$ equiv. cm³.	$KMnO_4$ lost cm³.
100	9·90	0,00	9·90	5	50	10·71	9·82	0·08
100	9·90	..	9·90	10	50	10.58	9·70	0·20
100	9·90	..	9·90	15	50	10·48	9·61	0·29
100	9·90	..	9·90	30	50	10·42	9·55	0·35
100	9·90	..	9·90	45	50	10·39	9·52	0·38
100	9·90	..	9·90	60	50	10·21	9·36	0·54
	$\frac{N}{10}CdCl_2$ cm³.							
100	9·90	..	9·90	5	50	10·35	9·49	0·41
100	9·90	..	9·90	5	50	10·39	9·52	0·38
100	9·90	..	9·90	10	50	9·70	8·89	1·01
100	9·90	..	9·90	10	50	9·75	8·94	0·96
100	9·90	..	9·90	15	50	9·31	8·53	1·37
100	9·90	..	9·90	15	50	9·43	8·64	1·26
100	9·90	..	9·90	15	50	9·50	8·71	1·19
100	9·90	..	9·90	15	50	9·52	8·72	1·18
100	9·90	..	9·90	30	50	9·39	8·61	1·29
100	9·90	..	9·90	45	50	9·36	8·58	1·32
100	9·90	..	9·90	60	50	9·07	8·31	1·59
100	25·00	..	9·90	60	50	7·34	6·73	3·17
100	50·00	..	9·90	60	50	4·64	4·25	5·65
100	[2 grms.]	9·90	9·90	60	50	0·81	0·74	9·16*

TABLE VI (continued).

Oxygen value $KMnO_4$=0·0003894 grm. per cm^3. Iodine value $Na_2S_2O_3$=0·005671 grm. per cm^3. 9·90$^{cm^3}$ $KMnO_4$=10·80$^{cm^3}$ $Na_2S_2O_3$. 1$^{cm^3}$ $Na_2S_2O_3$=0·917$^{cm^3}$ $KMnO_4$.

$\frac{N}{1}$HCl cm^3.	$\frac{N}{10}$$CrCl_3$ cm^3.	H_2O cm^3.	$KMnO_4$ cm^3.	Time digestion min.	Temperature C°.	$Na_2S_2O_3$ cm^3.	$KMnO_4$ equiv. cm^3.	$KMnO_4$ lost cm^3.
100	9·90	--	9·90	5	50	10·61	9·72	0·18
100	9·90	--	9·90	10	50	10·33	9·47	0·43
100	9·90	--	9·90	15	50	9·89	9·06	0·84
100	9·90	--	9·90	30	50	9·65	8·84	1·06
100	9·90	--	9·90	45	50	9.61	8·81	1·09
100	9·90	--	9·90	60	50	9·61	8·81	1·09
	$\frac{N}{10}$$MnCl_2$ cm^3.							
100	9·90	--	9·90	5	50	10·73	9·83	0·07
100	9·90	--	9·90	10	50	10·69	9·80	0·10
100	9·90	--	9·90	15	50	10·67	9.78	0·12
100	9·90	--	9·90	30	50	10·52	9·64	0·26
100	9·90	--	9·90	45	50	10·43	9·56	0.34
100	9·90	--	9·90	60	50	10·50	9·62	0·28
	$\frac{N}{10}$$MnSO_4$ cm^3.							
100	9·90	--	9·90	5	50	10·72	9·83	0·07
100	9·90	--	9·90	10	50	10·70	9·81	0·09
100	9·90	--	9·90	15	50	10·56	9·68	0·22
100	9·90	--	9·90	30	50	10·48	9·61	0·29
100	9·90	--	9·90	45	50	10·49	9·61	0·29
100	9·00	--	9·90	60	50	10·50	9·62	0·28

Here may be noted a greater loss of permanganate during equal periods of time with cadmium and chromic chlorides than with hydrochloric acid alone, the excess loss in the former case increasing with the time of digestion. This phenomenon is especially noticeable with cadmium chloride, and to determine whether this excess loss of permanganate is in any way proportionate to the amount of cadmium chloride used, amounts of this salt greater than that represented by 9·90$^{cm^3}$ of a tenth-normal solution were used. The result was as anticipated; the loss of permanganate increased with the increase in the amount of cadmium chloride used, until with 2 grams of this salt the

total $KMnO_4$ found showed a permanganate equivalent of only $0{\cdot}81^{cm^3}$ as indicated in experiment marked *. It would appear, therefore, that with cadmium chloride, and to a lesser extent with chromic chloride, the permanganate is reduced without leaving anything like a proportionate amount of chlorine in solution at the close of the hour's digestion. This may be due to reduction of the permanganate with liberation of oxygen, which does not act on the hydrochloric acid to produce chlorine, or to action of chlorine first liberated on the water giving oxygen. By either of these actions there would be a loss of the chlorine which goes to oxidize oxalic acid in Tables I to IV and to liberate iodine from potassium iodide in Tables V and VI. To ascertain whether this loss is occasioned by formation of oxygen, the following experiment was made: To 100^{cm^3} of normal hydrochloric acid were added 2 grams of cadmium chloride, 10^{cm^3} of water and the solution transferred to a 100^{cm^3} burette, enough water added to completely fill the burette, which required about 10^{cm^3} additional, and the burette inverted in a porcelain dish filled with water, the upper end of the burette being carefully stoppered. Almost immediately gas began to accumulate and continued to accumulate slowly for about three hours, at the end of which the permanganate color had disappeared. The amount of gas collected was too small to admit either of qualitative or quantitative tests with the crude apparatus here used. Additional experiments must, therefore, be made to determine definitely whether oxygen is evolved in this way. The evidence, however, so far as it goes, consistently points to evolution of oxygen in the interaction of hydrochloric acid and potassium permanganate in the presence of cadmium chloride. The author intends to investigate this point further, as well as the action of the other salts which Wagner regards as catalyzers. Gooch and Danner* have shown that oxygen is evolved from potassium permanganate acidified with sulphuric acid. Some such action, it seems, occurs in the experiments of this paper when permanganate is acidified with hydrochloric acid in the presence of cadmium chloride, part of the oxygen of the permanganate being evolved directly instead of liberating chlorine from hydrochloric acid, or the chlorine first liberated acting on the water to set free oxygen.

The author is indebted to Prof. F. A. Gooch for much advice and assistance in the preparation of this paper.

* This Journal [3], vol. xliv, 301 (1892).

ART. IV. — *Some Western Klamath Stratigraphy;* by OSCAR H. HERSHEY.

IN his paper in the May (1905) number of this Journal, Mr. J. S. Diller presents strong evidence in support of his contention that the Bragdon formation in northwestern California is a member of the Carboniferous series. Although I recognize that good paleontologic evidence must be the final arbiter in all discussions such as this concerning the Bragdon sediments, I am as yet not willing to fully accede to his conclusions, but without further field-work am unable to combat them. I make this explanation for the reason that this paper may appear to be an indirect reply to Mr. Diller, whereas it is an endeavor to record some important observations before the vividness of their memory be dulled by time.*

The objects of this paper are to introduce another formation from the Klamath region, and to show how thrust faulting may have given rise to apparently inexplicable problems in the geology of northern California.

The folding of the strata characteristic of the southern Klamath region is largely replaced northward by thrust faulting, breaking the rocks into four great eastwardly tilted fault blocks. Four important members of the fault system are now known. The most westerly was discovered and elucidated by Mr. Diller. It bounds the Klamath province on the southwest and is marked by the abutment of easterly dipping typical Franciscan sediments against the ancient schists of South Fork and Redwood Mountains; hence, it may be designated the Redwood Mountain fault. The next easterly (second magnitude faults ignored), which most directly concerns this paper, passes about two miles east of Orleans on the Klamath River, and may be known as the Orleans fault. The third has its finest development in Eddy gulch, near the Black Bear mine and postoffice and may be known as the Black Bear fault. In this portion of its course it dips easterly at a low angle, probably 15° or 20°, the ancient schists of the Abrams formation having been thrust for possibly five miles over on to the cherty shales considered of Devonian age; but in passing northward and southward it straightens up and becomes nearly or quite vertical, although for scores of miles it continues a prominent break in the strata. The fourth great fault is marked by eastwardly dipping sediments with strong Cretaceous characteristics apparently overhung by Devonian limestones and cherty

* Writing in the field, in eastern Nevada, without notes, maps or references, I must ask the reader's indulgence to informalities and to possible slight inaccuracies in figures.

shales, near the southern end of Scott Valley, as discovered by Dr. A. C. Lawson and the writer several years ago. This may be designated the Callahans fault.

These faults are profound breaks comparable with the first magnitude faults the world over, and may extend entirely through the Klamath province, although this is said with less confidence concerning the Callahans fault. The throw appears to be generally not less than a mile and may in many places exceed two miles, even where the dip is steep. The age as indicated in the case of the Redwood Mountain and Callahans faults by the strata involved, and perhaps in the Orleans fault by its persistent accompaniment by serpentine dikes, seems to be Cretaceous or later but not as late as the opening of the Quaternary, Indeed, it is my impression that on the south, Horsetown sediments lap across the Orleans and Black Bear faults without dislocation.

The territory to be especially considered lies along the Orleans fault for ten miles northerly and southerly from the Klamath River. Here it marks a remarkable change in the stratigraphy. I will first describe the rocks east of the fault.

With the exception of a small area of possible Salmon hornblende schist several miles south of the Klamath River, the formation first encountered east of the fault in the vicinity of Orleans is a great series of black shales, limestones and blue cherts which, for the purpose of this paper, I will designate the Blue Chert series, from its most characteristic constituent. This occurs in beds from fifty to several hundred feet in thickness, made up of thin regular layers. The prevailing dark blue-black color seems to have been bleached in places, some outcrops having a whitish or light gray color. Also, isolated areas of very limited extent possess red chert very closely resembling typical Franciscan chert; the invariable presence of igneous rock suggests reddening of the blue chert by heat. Between the chert beds are somewhat thinner layers of soft black shale, much of which has been crushed to a schistose structure. The limestones occur in small lentils, either isolated or developed along certain lines parallel to the strike of the shales. They probably represent definite horizons, of which there may be several in the series. They are generally thoroughly recrystallized and without recognizable fossils. Indeed, the only fossils known between the Orleans and Black Bear faults, in the Salmon River basin, which is largely occupied by this series, are radiolaria in the cherts. The age, therefore, can only be determined upon lithologic grounds. It is presumed to be Devonian because similar rocks elsewhere in the Klamath region carry Devonian fossils.

The peculiar bluish bedded cherts occur throughout the area of outcrop of this series, but in some localities are more strongly developed than in others. They are especially prominent south of the Black Bear mine, where I estimate the thickness of the formation to be about 5000 feet, of which probably 3000 feet is chert.

Beginning at the Orleans fault, two miles east of Orleans, and proceeding thence up the valley of Pearch Creek, climbing the western flank of Orleans Mountain, we find first a belt of quartz schist (produced by the shearing of chert) and associated with it lentils of limestone, the whole dipping easterly 45° to 60°. This is succeeded by ordinary cherts and shales in alternating layers, all dipping eastward at angles not less than 30°. But the formation has been very thoroughly shattered by the intrusion of igneous material. In places, this occurs in a network of small dikes traversing the sedimentary rocks in all directions; in others it is in large masses almost excluding the shales and cherts. Inclusions of the latter are exceedingly common and vary in size from infinitesimal fragments to masses a quarter of a mile in length. All the larger fragments more or less preserve the original easterly dip. By means of them one can trace, in Pearch Creek valley, the outlines of a succession of strata at least 3000 feet thick, everywhere dipping easterly at a comparatively steep angle.

This thorough intrusion of the Blue Chert series by apparently dioritic and diabasic material is general throughout its extensive outcrop areas in the western Klamath region. Probably no quarter section of it is without these dikes and in many square miles there is much more igneous than sedimentary rock. I want to strongly impress the fact that this intrusion is not local.

In Pearch Creek valley, the intruded igneous material appears to pass upward into a volcanic series of andesites and rhyolites, which, if I rightly remember, is 800 to 1200 feet thick. An important member in the lower part of the series is an andesite characterized by small block-like crystals of hornblende probably originally a pyroxene. This may be partly in the form of large dikes penetrating deep into the complex of sedimentary and intruded rocks, but it also spreads out in the form of a thick sheet. The upper portion of the series consists of gently dipping beds of white rhyolite, some of which is fragmental, suggesting tuffs. Specimens of different phases were submitted to Mr. Diller for microscopic examination and he conceded the probability of this being a volcanic series. Certainly its attitude and texture oppose the idea of its having been intruded beneath the great thickness of sedimentary rocks above it.

The volcanic series dips at a much lower angle than the Blue Chert series beneath it, suggesting marked nonconformity by reason of pre-volcanic uplift and great erosion. Elsewhere in the western Klamath region masses of volcanic rocks rest nonconformably on the Blue Chert series. I have never seen any evidence of volcanic rocks interbedded with this series. In one place, below Cecilville in the valley of the South Fork of Salmon River, tuffs and lavas occur under Paleozoic limestone and chert, but the contact is a nonconformity reversed by overturning. It is my impression that in the western portion of the Klamath region, all the clearly volcanic rocks are younger than the Devonian Blue Chert series.

Above the rhyolite in Pearch Creek valley, there is a formation of black slaty shale whose maximum thickness I estimate at 3000 feet. At the base there is a slight development of coarse sandstone, apparently made up of debris from the underlying quartz-bearing rhyolite. It hardly anywhere attains a thickness of 50 feet, but may be traced along the contact for several miles; and there is little doubt of its having been laid down on the surface of the volcanic series. I have found no evidence of nonconformity at this contact and it is my impression that the deposition of the sandstone followed closely that of the rhyolite.

Excepting this thin basal sandstone, the formation contains no conglomerate, sandstone and limestone, and only a few thin layers of chert. Its most characteristic feature is that it is largely composed of layers of the thickness of coarse paper. It resists weathering so well that it stands in high rugged ridges and peaks, often bare of soil, and having a rusty color on outcrop. The reddish brown high ridge at the head of Pearch Creek, a prominent feature in Orleans scenery, is largely of this formation.

So far as known, it is confined to a basin-like depression in the surface of the older rocks, in an area possibly 20 miles long (north-south) and 10 miles wide, lying west of Know-nothing Creek, south of Salmon River, east of the Orleans fault and north of "Trinity Summit." As the valley of Nordheimer Creek is largely cut in it, I propose to designate it the Nordheimer formation.

Its dips are prevailingly toward the center of the basin but usually not at high angles, contrasting with the dips of the Blue Chert series lower. Their relation is certainly that of marked nonconformity although they are separated by igneous rocks.

The Nordheimer formation is badly shattered by intrusive rocks. They are clearly plutonic, being largely in the form of batholithic masses of gray and greenish, fine-grained crystal-

lines, probably in part metagabbro, diabase and diorite. In part of the area that properly belongs to the Nordheimer, the shale exists only as large inclusions. Ten miles south of Orleans, the plutonics have so thoroughly usurped the area that I gave up tracking the shales. These igneous masses must extend down into the Blue Chert series, but there is also a great amount of igneous material in the latter that has no representative in the Nordheimer. I am compelled to admit that the western portion of the Klamath region has had at least two marked epochs of igneous activity between early Devonian and late Jurassic times.

No traces of fossils having yet been discovered in the Nordheimer, its age can only be conjectured. It may be late Devonian, but that would imply a strong nonconformity in the Devonian series. It is more likely Carboniferous. Some of its characters suggest the Baird formation. It might also be a western representative of the Triassic Pit shales, but it is not likely to be any younger. These suggestions show that there is nothing definite upon which to base an argument as to its age.

On the western side of the fault, a belt from four to seven miles wide is occupied, so far as sediments are concerned, by a series which I have heretofore described as a portion of the Bragdon formation. It is about 5000 feet thick and consists of a rapid alternation of soft black slates (produced by the shearing of thin-bedded shales) and of gray crushed coarse sandstones. The latter occur from top to bottom of the formation and it is difficult to determine that they are more abundant in one quarter than in another. The coarser grains are largely various colored cherts like those common in the Bragdon conglomerates of the eastern area. In fact, this alleged western Bragdon is identical in essential characters with the eastern Bragdon except that the conglomerates of the latter are here replaced by coarse sandstones, and that it is more highly altered by shearing. I have treated the subject at such length in former papers on this region that it is unnecessary to repeat the comparison any further. Perhaps this western formation is not the Bragdon, but I am as yet so far from convinced of it that I will continue to refer to it under that name; at any rate, its identity with the original Bragdon is not essential to this paper. It has yielded no fossils except some apparent seaweed impressions several miles north of Orleans.

The original bedding planes are clearly apparent in the Orleans region so that there is no difficulty in determining the structure. In the central portion of the belt it lies at low angles, inclined to form a slight syncline. Within a quarter of a mile of the fault, near the Klamath River, it dips steeply

eastward, bent down by the thrust. Farther south the strata come up with nearly horizontal attitude to the almost vertical fault plane, leaving no doubt of the reality of the fault.

In approaching the western border of the belt, the strata are bent up and presently there appears under them a formation made up of white sericitic and green chloritic schists that are evidently sheared rhyolites and andesites. In a very short distance another fault brings down the Bragdon slates. This may be repeated several times in 20 miles, but far the larger portion of the area is Bragdon. The shearing becomes more pronounced toward the west until traces of the bedding planes are virtually destroyed. I now consider the Weitchpec schists, formerly classed as pre-Bragdon, as a portion of this series. Indeed, the apparent ancient schists of Redwood Mountain on the Korbel-Hoopa trail are probably Bragdon, although undoubted pre-Devonian schists occur in South Fork Mountain. The fact is that the Bragdon spreads over an immense area west of the Orleans fault, running as a broad belt far to the north and as a narrowing belt (in places several belts) southward to the Sacramento Valley. Along the trail from Orleans to Hoopa, one is scarcely off it except when on serpentine.

Wherever the base of this western Bragdon is exposed, it is underlaid by igneous rocks which have characters suggesting a volcanic series. In addition to fragmentals (which appear to be tuffs) and vesicular lavas, the other textures and structural relations of the members certainly oppose the idea that they have been intruded under 5000 feet of sediments. No dikes rise from the igneous rocks into the slates and there are no inclusions of the latter in the former. Furthermore, the slates pass so readily from contact with one to that with another member as to suggest an erosion interval between the two formations.

Below the volcanic series there is a great complex of intruded igneous material and of shales, bedded blue cherts and limestones identical in character with the Blue Chert series east of the Orleans fault. Its outcrop begins west of Hoopa Valley as a narrow belt and extends southward, gradually widening, to the border of the Sacramento Valley. The limestone lentils which it contains are in places quite fossiliferous, containing, if I remember rightly, early and middle Devonian faunas.

Thus we seem to have on both sides of the Orleans fault a great series (or two lithologically identical series) of shales, cherts and limestones that has everywhere been excessively intruded by igneous material. Over the complex is volcanic rock that may represent two formations on opposite sides of the fault, possessing similar characters. Over this is altered shale thousands of feet thick. *But the upper sedimentary*

formation east of the fault is not the same as the upper formation west of the fault. Which is the older?

It is beyond question that the Bragdon and Nordheimer cannot be equivalents. The plane of the Orleans fault is so steep that the horizontal displacement cannot exceed half a mile. Five miles south of Orleans, the two formations would contact along the fault if the serpentine dike were absent. Equivalence would imply that a formation which preserved its character of alternating sandstone and shale over an area at least 20×50 miles, within half a mile lost all its sandstones except the basal one, and then preserved invariable its new character over 10×20 miles.

The Bragdon formation comes up to the Orleans fault on the west along a distance exceeding 50 miles, but no trace of it has been found east of the fault short of the "eastern Bragdon area." The Nordheimer formation comes up to the fault on the east, but has never been identified west of it. Yet within two miles these formations have thicknesses respectively of 5000 and 3000 feet. There certainly is here a problem worth considerable effort to solve.

If faulting had not occurred, it is probable that the two formations would somewhere be found in original contact. If the Nordheimer is the older, it is probable that a portion of it is buried under the Bragdon just west of the fault. If the Bragdon is the older, it was removed by erosion previous to the deposition of the Nordheimer east of the fault or else it lies under the Blue Chert series, a very remote possibility. The latter would imply that there are two cherty series of identical characters and three systems of intrusive material.

The Bragdon is more highly altered by shearing than is the Nordheimer, but that is no criterion of relative age. The Bragdon was softer and less able to resist a shearing stress. Besides, the dynamical action operated only in the territory west of the fault.

But there is one feature about this western Bragdon which makes it practically certain that it is younger than the Nordheimer. *It is absolutely without a trace of any intruded igneous material other than granite and serpentine* (originally peridotite chiefly). I made a similar statement in connection with the "eastern Bragdon area" and Mr. Diller has taken exception to it, so to be cautious I will modify the above statement as follows: In the course of several hundred miles travel in the western Bragdon area I have never observed any evidence of intrusive rock except a few small masses of granite and a few serpentine dikes, the latter usually on the borders. This does not mean that within the Bragdon area there are no igneous rocks other than those mentioned. In going west-

ward one will frequently arrive at a point where the strata bend up and presently igneous rocks appear. They usually have the characters of surface volcanics and always are in belts parallel to the strike of the slates and sandstones. Such features as I usually accept as criteria in the determination of the fact of intrusion in the Blue Chert and Nordheimer formations are positively absent here. Even these igneous rocks do not appear in the 4- to 7-mile belt of pure Bragdon next to the Orleans fault. I have gone 12 miles north from Orleans without seeing anything but Bragdon and have had similar experiences on long trips in other directions. The significance of this will be apparent when I say that in the course of several hundred miles travel in Blue Chert areas and several score in the Nordheimer area, I have probably not for any five minutes been out of sight of nearby igneous rocks.

The only theory in explanation of this distribution of the intrusives which seems to me to have a natural ring is that at the time of their formation (granite, peridotite and all later igneous rocks excepted), the Bragdon formation of the western area was not in existence. Otherwise, the igneous material has exercised a most remarkable selection. I am aware that intrusives will to a certain extent concentrate into certain formations which are most easily penetrated, but this objection does not apply in this case. There is nothing about the Bragdon to make it especially resistant to melted rock. On the contrary, it is the softest and most easily broken formation of pre-Cretaceous age in the Klamath region west of the Sacramento River. Granite and peridotite found little difficulty in cutting through it. My observation of intrusives in other regions such as eastern Nevada lends no encouragement to the idea that the Bragdon resisted the penetration by such material as intimately injected every other formation of the region.

The hypothesis of "localization" is not pertinent because we are dealing with a territory several thousand square miles in extent and an asserted contrast which is not based on very limited observation. Remember, we have on one side tens of thousands of dikes and scores of large batholiths and on the other side nothing.

If the Bragdon formation goes down under the Blue Chert series east of the Orleans fault, it must necessarily be intimately intruded by the igneous rock which is so abundant in all parts of the other series. This would break down any theory based on an alleged resistance to intrusion and would make it unreasonable to suppose the intrusives rapidly gave out in the half mile accounted for by the fault. (This fault is far younger than any igneous rock entering into this discussion.) Therefore, it appears to me improbable, almost to the extent of cer-

tainty, that the Bragdon formation is older than the Blue Chert series east of the fault and its superposition proves that it is younger than the similar series west of the fault.

In the case of the Nordheimer and Bragdon we have two areas of shales practically adjoining, one badly shattered by a certain system of intrusives and the other entirely free from them. It would seem to be ignoring very strong evidence to fail to consider the Bragdon the younger.

Within several miles east of the Orleans fault, extending from Patterson's in the valley of New River, to Hall City, there is a succession of limestone outcrops from which Mr. Diller's party and the writer have collected fossils representing a very late Carboniferous or perhaps Permian fauna. Associated with the limestones are shales not very greatly differing from the shales of the Blue Chert series. It is my impression that this late Carboniferous or Permian series is just as thoroughly intruded by igneous material as the Blue Chert and Nordheimer formations; but I regret that a lack of opportunity to visit the belt during the past few years prevents me from basing this statement on clear mental pictures of igneous rocks cutting the fossiliferous limestone. However, I distinctly remember that the belt containing the late Carboniferous or Permian rocks, especially in the New River country, contains more than the usual amount of igneous material, largely in the form of small batholiths. The Bragdon area, a few miles west, has none of them (serpentine, granite and later intrusives excepted).

Between the Blue Chert series, which I have decided must be pre-Bragdon, and the late Carboniferous or Permian rocks there is nothing suggesting the Bragdon formation and no fault or known interval of deposition to account for its absence. However, the country has not yet been so thoroughly explored as to give this argument conclusive value. I am not endeavoring to settle the question now, but to show that all the known evidence points strongly to the Bragdon formation of the western area being younger than the Blue Chert series, younger than the Nordheimer formation, even younger than the late Carboniferous or Permian limestone.

Sept. 30, 1905.

Art. V.—*A Study in the Metamorphic Rocks of the St. Francis Valley, Quebec;* by John A. Dresser.

The Quebec group as originally defined embraced several comparatively narrow belts running parallel to the folding of the Appalachians throughout the extent of that system in Canada.* They were found to consist of much altered strata of Cambro-Silurian age, which had been deposited under peculiar conditions such as to strongly distinguish them from normally deposited strata of the same age. In structure they were thought to generally form synclinal folds, often highly distorted and overturned. All lay to the east of the dislocation running from the northern end of Lake Champlain to the St. Lawrence river in the vicinity of Quebec city, which is known as the Champlain and St. Lawrence fault.

It was subsequently ascertained† that within the Quebec Group thus defined there had also been included certain older measures belonging to the Cambrian and Precambrian systems, and also frequent and extensive masses of ancient and highly altered rock of volcanic origin,‡ whose igneous character had not been previously recognized. Accordingly, in the re-examination more recently made by the Geological Survey of Canada,§ these rocks along with certain of the associated volcanics have been separated from the Quebec Group, but the progress of geological investigation has not yet admitted of a very detailed subdivision.

The most extensive of the older belts thus brought to light is that which comprises the Sutton Mountain anticline, fig. 1, the course of which, in common with the other principal axes of the Appalachians is a northeast-southwesterly one. Near the St. Francis river, which crosses it about at right angles, it is rather less than six miles wide, including a small band of Trenton whose position within the older measures has been hitherto explained as "due to an intricate system of folding and faults."‖

A section across the Sutton Mountain series and the included

* "Geology of Canada," 1863, pp. 225–297, Sir W. E. Logan.

† "The Quebec Group in Geology," Transactions of the Royal Society of Canada, vol. i, 1882, Dr. A. R. C. Selwyn.

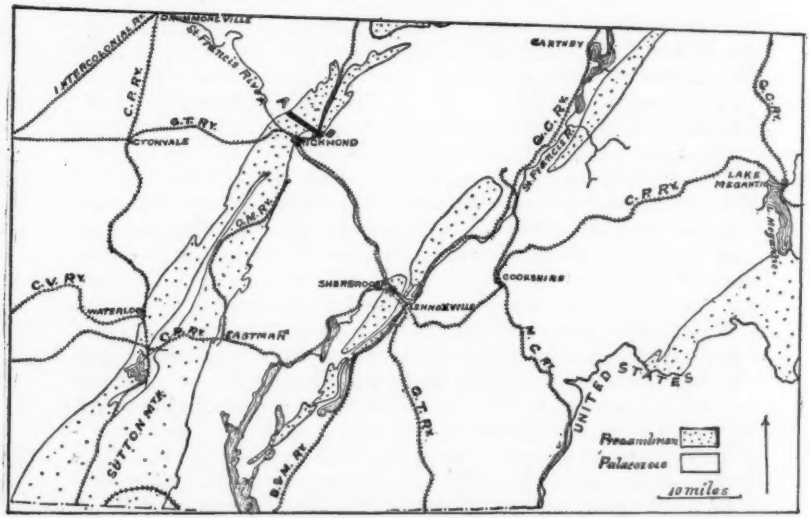
‡ "Notes on the Microscopic Structure of some Rocks of the Quebec Group," Report Geological Survey of Canada, 1880–1–2. Dr. F. D. Adams, "The Quebec Group," Appendix A to Harrington's "Life of Sir W. E. Logan," by Sir J. W. Dawson, 1883.

§ Annual Reports Geological Survey of Canada, 1880–1–2, and 1887–8, Dr. A. R. C. Selwyn; 1886, 1887–8 and 1894, Dr. R. W. Ells.

‖ Ann. Report Geol. Survey, 1886, p. 18 J.

Trenton in the vicinity of Richmond* forms the subject of this paper. The line of the section extends between lots ten and twenty-seven in the twelfth range of the township of Cleveland, and is about a mile and a half east of the St. Francis river, to which it is approximately parallel. The direction of the sections is N. 38° W., magnetic. The adjacent rocks at both north and south have been recently mapped in the reports of the Geological Survey as Cambrian, the black limestone, No. 3 of the section, as Trenton, and the rest as Precambrian.

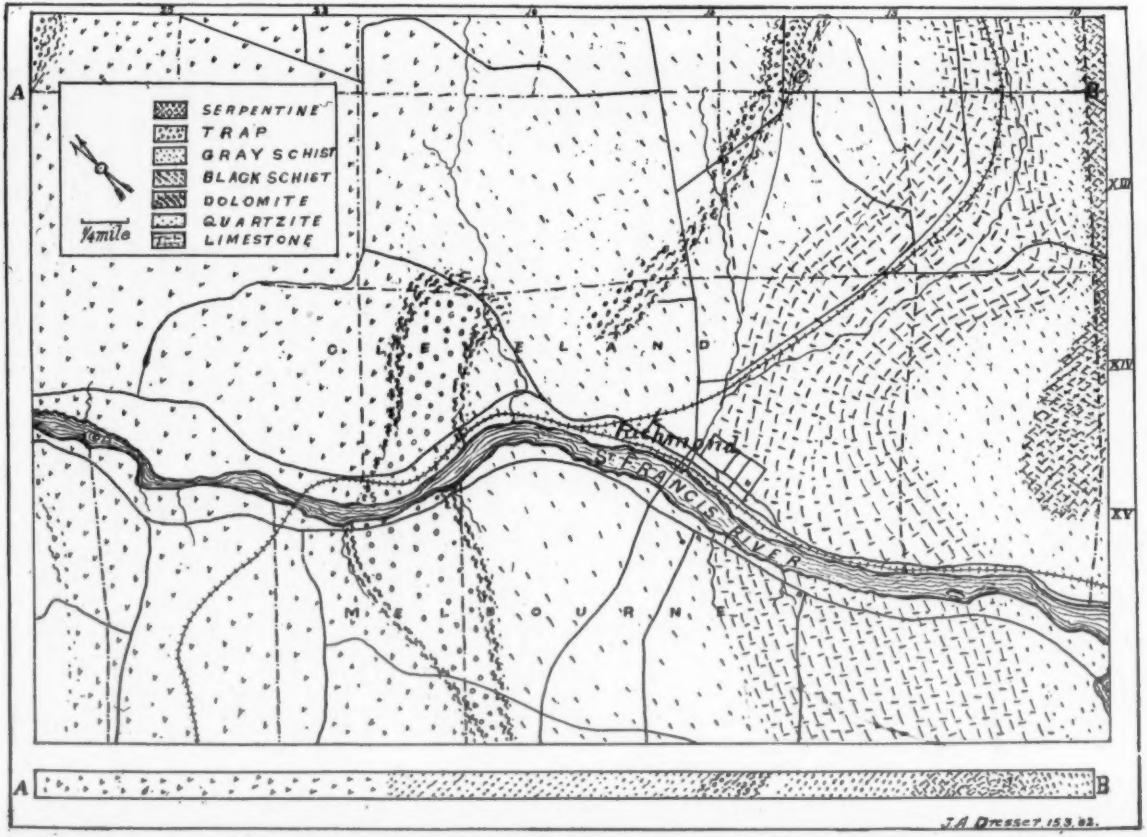
1



Sketch map showing the Precambrian of a portion of Southeastern Quebec as designated on the Geological Survey maps of 1886 and 1894.

1. Black Mica Schist	100	feet
2. Gray Mica Schist	1320	"
3. Black Limestone	2800	"
4. Gray Mica Schist	4590	"
5. Micaceous Dolomite	300	"
6. Black Mica Schist	600	"
7. Quartzite	180	"
8. Micaceous Dolomite	60	"
9. Gray Mica Schist	7360	"
Total Sedimentary	17310	feet
10. Amygdaloidal Trap, Total Igneous	12540	"

* This locality was considered by Logan to furnish the key to the structure of the Quebec Group. Hither he returned after severing his connection with the Geological Survey, and spent four seasons in making a detailed map of the district for about five miles on either side of this section. This map, which seems to have been ready for engraving at the time of his death, was unfortunately, never published.



Map and section across the Sutton Mountain Series near Richmond, Quebec.

LITHOLOGY.

Black (Graphitic) Limestone.—This is a very dark gray, or more frequently, a black impure limestone carrying a large proportion of graphite, which is sometimes so great in amount as to give the rock somewhat of the unctuous feel of that mineral. It is consequently very soft and brittle. It is usually much wrinkled and corrugated by pressure and not infrequently has a distinct slaty structure developed at high angles to the bedding plane. It contains numerous veins of crystalline calcite and quartz, in which cases these minerals are intricately associated in the same veins without any discernible arrangement. Some of the veins carry a little pyrite.

At Melbourne village, opposite the town of Richmond, this rock is marked as fossiliferous on the Montreal sheet of the Eastern Townships map issued by the Geological Survey to accompany the Annual Report of 1894, but no determination of the fossils or indication of their age is recorded except that the notation of the map includes the rock with the 'Farnham Black Slates' of the Lower Trenton formation, $D3^a$.

Gray Mica Schist.—This is a schistose rock, usually much wrinkled and contorted, and cleaves very smoothly in the most intricate folds. In color it is a light or greenish gray, weathering to dark gray, or brown, tints.

Under the microscope it appears as a rather fine even-grained and much altered sandstone with a highly developed schistose structure. The grains are both feldspar and quartz and are contained in a micaceous (sericite) cement in which chlorite occurs in varying amounts. A little iron ore is present in small grains, or string-like masses, and also occasional cubes of pyrite of microscopic size. It is an undoubted clastic.

Black Mica Schist.—By an increase of dark minerals, chiefly iron, and probably by the addition of graphite, the gray mica schist passes into a black schistose rock having a submetallic lustre on its cleavage faces. Microscopically it differs little from the previous rock except in the dissemination of dark grains of the opaque minerals. In reflected light some of the larger can be easily distinguished as pyrite, or a black ore of iron, but others, the smaller and more numerous which are irregular in outline, are thought to be graphite, in part at least. The gravity of the rock is not such as to indicate any noticeable increase in heavier constituents over the preceding variety.

Occasional inclusions of dark gray or black limestone are found in the black mica schist. They vary in size from mere grains to masses several feet in each dimension. It is difficult to estimate their proportion in the rock, as they agree with it very closely in color and share in its foliation. They are not

numerous enough to warrant calling the rock a conglomerate in the usual sense of the term, yet they are quite distinct in lithological character from the enclosing rock. One of these, which occurs on Lot 15, Range xiii of the Cleveland, can be seen to occupy not less than four hundred feet, and may be considerably more extensive. Its thickness could not be ascertained, but is not less than two feet. Similar occurrences of limestone are also found in the micaceous dolomite and will be subsequently noted.

As there is no evidence of concretionary structure they must apparently be either fragments of an earlier and distintegrated limestone bed, or calcareous deposits formed contemporaneously with the enclosing rocks. The absence of any evidence of unconformity or other indication of a time-break favors the latter view.

Micaceous Dolomite.—The gray mica schist becomes dolomitic in certain parts by the intercalation of lenses of magnesian limestone. These growing more abundant and the intervening bands passing into an impure earthy magnesite, the rock eventually becomes a crystalline dolomite. In the hand specimen it is fawn-colored and shows the presence of quartz on the weathered surface. In the thin section it is made up of crystalline dolomite with about one-quarter of the slide occupied by quartz. The latter is generally well crystallized, showing that it was formed not later than the dolomite. The débris of a kiln where the dolomite was formerly burned for lime, as well as decayed portions of the rock, yield considerable numbers of well-formed, transparent quartz crystals.

Lenticular masses of rich hematite ore carrying octahedral crystals of magnetite occur in the dolomite at various places. They are found several feet in thickness and are either overlapping or nearly continuous for distances of a mile or more. Their close association with dolomite suggests their origin from altered carbonates.

The dolomite also contains pure limestone masses, as noted above, one or which is of much importance from the fact that it has long been known to contain fossils. This mass, which is found on Lot 14 in Range xii of the township of Cleveland, about three hundred yards east of the Healy schoolhouse, is some two feet in thickness and thirty in length as exposed on the face of a low escarpment of dolomitic mica schist. A cummunication from the late Sir William Dawson on the silicification of these fossils appeared in the Quarterly Journal of the Geological Society of London in the year 1879.* In this they were referred to as of Lower Silurian age and the genera Steno-

* "On Paleozoic Fossils mineralized with Silicates," Q. J. G. S., Feb. 1879, pp. 60–62.

pora and Ptilodictya are mentioned, but no more definite description seems to have been yet published.

Quartzite.—With the increase of quartz, the dolomite passes into a calcareous sandstone and eventually to a somewhat impure quartzite. This consists of rounded quartz grains, a few grains of feldspar, and where the rock is much deformed by pressure, or else where the original composition was slightly different, shreds of sericite are developed along the planes of foliation. The chief cementing material in typical parts has been silica, and the enlarged grains thus assume irregular interlocking forms.

A few rather large grains of feldspar, either orthoclase or microcline, are generally found in the thin section as well as occasional ones of a rhombohedral carbonate, probably dolomite. This rock is commonly interbedded with black mica schist in an intricate manner, apparently indicating transitional phases between the two classes of rocks.

Amygdaloidal Trap.—The volcanic nature of this rock, which was formerly regarded as an argillite or was more frequently designated as a chloritic schist, has been preliminarily noted* by the writer, but opportunity has not yet been found to complete a petrographical examination of it. It is a bluish or greenish gray rock, in some places massive, and is often highly schistose. It contains large numbers of vein-like masses of quartz and some of calcite, is amygdaloidal in many parts, and frequently contains nodular masses three or four inches in diameter which are composed chiefly of rudely concentric layers of quartz and epidote.

By the aid of the microscope, crystals of primary plagioclase can be seen whose arrangement is suggestive of the structure of diabase, but as the interstitial material is wholly secondary, chlorite, iron ore, leucoxene, etc., further evidence is desirable in order to determine its precise classification. It appears to have been somewhat variable in its original character, as fibrous hornblende occurs in considerable amount at a point about three miles west of the St. Francis river, but it may be generically classed as a basic volcanic of the andesite or diabase class. It has been extremely altered.

Structure.

The *contacts* of the various sedimentary rocks with one another are, as has been already stated, of the nature of transitions from one to another of the different types. The graphitic limestone passes upwards into mica schist by an almost insensible gradation, as can be well seen along either bank of

* The Ottawa Naturalist, January, 1901; this Jour., July, 1902.

the St. Francis river in the town of Richmond, or the village of Melbourne. Perhaps better evidence still is to be found in the banks of the little post-glacial gorge of the "eddy" brook in Melbourne. Here in a height of about thirty feet the rock passes from typical black limestone in the bed of the stream to black mica schist at the top of the northern bank, which owes the steepness of its slope in some measure to the differential resistance to erosion in the various strata exposed in it. Somewhat similar phenomena can be seen in the Cushing brook in Richmond, where, however, the banks are not as high. In both cases the strata dip towards the north-northwest at an angle of probably less than 30°. On the western bank of the St. Francis river* the black mica schist, which forms the transitional beds between the black limestone and the gray mica schist, contains interbedded lenses of quartzite, an association that is common in another part of the section where these two rock varieties have their chief development. The gradual passage of mica schist into micaceous dolomite and of the latter into quartzite has been already mentioned. Hence it appears conclusive that the stratified rocks of this section belong to a single cycle of deposition.

With regard to their relation to the igneous rocks in point of age, the balance of evidence thus far obtained indicates that both igneous masses are older than any of the intervening sediments. At the south the evidence is not conclusive, being wholly negative, viz., the absence of dikes, contact metamorphism, springs along the contact, or other phenomena characteristic of an intrusive contact. On the north the case is a clearer one. Besides negative evidence similar to the above, the dolomite where it approaches the trap in the township of Melbourne holds fragments of the latter rock. Also the gray mica schist on the line of section shows a marked increase in the amount of chlorite which it contains as the trap hills are approached. This is so noticeable as to make the rock difficult to distinguish from the trap in the field near the contact. As the latter is a rock that reduces to a fine debris of which chlorite is the most conspicuous mineral, this phase of the mica schist appears to have derived its character from the residual material of the trap. It is thus equivalent in evidence to a basal conglomerate.

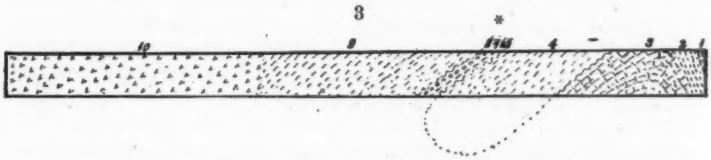
The *dip* is naturally regarded as an observation of, at most, very doubtful value in such a highly disturbed region, unless corroborated by other evidence.

In *stratification* all the rocks on the north of the black limestone appear to dip towards the northwest, and those on

* The old ferry landing at the rear of the residence of Mrs. J. Dunbar.

the south in the opposite direction, or about southeast. The limestone would thus form the axis of the anticline. This view was held by Logan, while Ells takes the ground that the limestone is of much more recent formation than the other rocks of the section and has been infolded into its present position, but just in what manner has not been explained, otherwise than as by "an intricate system of folding and faults." The former placed all these rocks in the Quebec Group, of Calciferous-Chazy age, while the latter regards the limestone as Lower Trenton and all the other rocks as Precambrian.

While Logan believed all the rocks of this section to be of sedimentary origin, and also included the serpentine belt at the south in the same class, correlating it with the dolomite on the ground of the magnesian character of each, Selwyn and Ells recognized the igneous origin of the serpentine, but still included the twelve thousand feet, or more, of trap in the



northern part of the section with the clastic rocks. Hence the results of both investigations may be reasonably submitted for reconsideration.

There appears to the writer no reason to believe that there was any great time-break in the deposition of the sedimentary rocks of this section. The contacts are transitional and the black limestone has suffered from dynamic metamorphism no less than the mica schists.

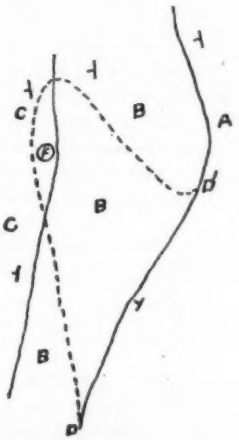
It is, moreover, an apparent fact that the dolomitic schist cannot be referred to the Precambrian from the presence of the fossils already referred to in the non-magnesian limestone masses included in the dolomite. The importance of this isolated occurrence of fossils in the dolomite seems to have been lost sight of in the more recent work of the Geological Survey, by the exposure having been erroneously connected with the black limestone three-quarters of a mile distant. For in the Sherbrooke and Montreal sheets of the Eastern Townships map of the Geological Survey of Canada (1886-1894), the locality of these fossils, Lot 14, Range xii of the township of Cleveland, is included in the Trenton area by a peculiar indentation, D-D fig. 4, in the part colored Precambrian, the boundaries of which are thus made to cross the actual stratification of the

* Fossils at this point.

rocks. The part of the dolomite, "B," immediately surrounding the locality of the fossils, and the intervening mica schists are accordingly colored Trenton in Lots 13, 14 and 15 in Ranges xii and xiii, while they, "B-B," are elsewhere mapped as Precambrian in either direction along the strike.

The *order of deposition* which best explains the structural features appears to be as follows, in ascending series:

4



A. limestone, Trenton or Black River
B. mica schist } mapped as Precambrian
C. dolomite } except within the line D-D'
F. fossils
γ. strike and dip--40°.

1. Black limestone, with black mica schist as its marginal or shallow-water equivalent.

2. Quartzite, quartzose and micaceous dolomite, which were chiefly deposited in the northern part of the section and barely extend to the northern side of the present exposure of the black limestone.

3. Gray or green mica schists covered the entire trough between the preëxisting igneous ridges.

Two causes present themselves to account for the real or apparent greater thickness of these schists towards the north. If, as the position of the locality with reference to the main ridges of the Appalachian uplift indicates, the Lower Silurian transgression come from the north, the original thickness probably was really greater in the northern than in the southern part of the section. Or, since all these clastics after their

deposition were crushed between the heavy masses of igneous rock on either side, an apparent thickening would naturally be produced by a succession of thrust planes, which owing to the homogeneous character of the rock would not be easily distinguished from ordinary cleavage planes. It has been shown experimentally by Cadell* that a "compressed mass tends to find relief along a series of gently-inclined 'thrust planes' which dip towards the side from which the pressure is exerted." This tendency, which was cited in explanation of the abnormal thickness of the Silurian quartzites, shales and limestones of Sutherlandshire, Scotland, seems quite applicable to the present case, where the conditions are essentially those which Mr. Cadell's experiments were designed to reproduce. The uniform cleavage, which dips towards the northwest at an angle of rather less then 40° for some three and a half miles, may be then merely one effect of a pressure exerted from the St. Lawrence valley in the process of the Appalachian uplift.

Summary.

The results of this study are therefore to show,

1. That the rocks of the Sutton Mountain anticline contain no Precambrian clastics (Algonkian), in the vicinity of the St. Francis river.

2. That Paleozoic (Quebec Group) sediments occupy a trough between two earlier igneous ridges, viz., the serpentine at the south and the trap on the north, the latter of which has not been hitherto recognized in structural examinations of the locality.

3. That the Precambrian of the region, if any, is thus confined to the volcanics, whose age has not yet been further investigated since their eruptive origin has been known.

Montreal, Canada.

* Transactions of the Royal Society of Edinburgh, 1888. "Experimental Researches in Mountain Building," H. M. Cadell.

SCIENTIFIC INTELLIGENCE.

I. Chemistry and Physics.

1. *The Hydrides of the Alkaline Metals.*—Having previously prepared and described the colorless, crystalline hydrides of potassium and sodium, KH and NaH, Moissan, in continuing this line of work, has found that hydrides of cæsium and rubidium exist, CsH, and RbH, and that these have entirely similar chemical and physical properties. The author gives some general reactions of these interesting compounds. They are all powerful reducing-agents, and decompose water in the cold with the evolution of hydrogen:

$$RH + H_2O = ROH + H_2.$$

They decompose also the hydrogen acids:

$$RH + HCl = RCl + H_2$$

$$RH + HCOOH = HCOOR + H_2.$$

They react with gaseous ammonia:

$$RH + NH_3 = NH_2R + H_2.$$

When heated very gently in the presence of carbon dioxide they yield alkaline formates:

$$RH + CO_2 = HCOOR$$

and upon slightly raising the temperature they give mixtures of formate and oxalate:

$$2KH + 2CO_2 = K_2C_2O_4 + H_2.$$

Further, an alkaline hydride when heated in an atmosphere of carbon monoxide gives a slight deposit of carbon, and is partially transformed into formate:

$$2CO + KH = HCOOK + C.$$

Sulphur dioxide reacts at ordinary temperatures, under certain conditions of pressure, with the production of hydrosulphites:

$$2RH + 2SO_2 = R_2S_2O_4 + H_2.$$

Certain organic compounds containing halogens react with the alkaline hydrides at temperatures above 150°:

$$RH + C_2H_5I = C_2H_6 + RI;$$

$$RH + CH_3Cl = CH_4 + RCl.$$

In contact with cyanogen gas in the cold they give cyanides and hydrocyanic acid:

$$RH + C_2N_2 = RCN + HCN.$$

With acetylene at ordinary temperatures the following reaction takes place:

$$2RH + 2C_2H_2 = C_2R_2.C_2H_2 + 2H_2,$$

and, when gently heated, the double compound gives off acetylene and leaves a carbide, C_2R_2.

The author has shown, further, that the alkaline and alkaline earth hydrides do not conduct electricity and cannot be classed with the alloys. Consequently, in its combinations hydrogen ought not to be considered as a metal.—*Ann. Chim. Phys.*, VIII, vi, 289. H. L. W.

2. *The Boiling-points of the Alkaline Metals.*—On account of experimental difficulties, the boiling points of sodium and potassium have not been accurately determined, and no attempts have been made to determine this constant for lithium, rubidium and cæsium. RUFF and JOHANNSEN, having found that the vapors of these metals do not act upon metallic iron, have distilled the metal in wrought-iron retorts consisting of long tubes enlarged at the bottom, and have measured the temperatures of the vapors by means of a thermo-electric couple protected by a steel tube and introduced into the vapor. Accurate results were apparently obtained in all cases except that of lithium, which boils at too high a temperature for the application of this method. The boiling-points found were as follows: cæsium, 670°; rubidium, 696°; potassium, 757½°; sodium, 877½°; lithium, higher than about 1400°. When these boiling-points are plotted with the atomic weights a curve is produced which slowly rises from cæsium, through rubidium to potassium, then becomes steeper to sodium, and finally rises very steeply to lithium. The curve is quite similar to that of the melting-points, but it does not permit the calculation of the boiling-points as a function of the atomic weights by means of a simple mathematical formula.—*Berichte*, xxxviii, 3601. H. L. W.

3. *The Rusting of Iron.*—The slow oxidation of iron at ordinary temperatures was at first regarded as a simple process, but more recently iron has been generally supposed to rust through the combined action of carbon dioxide, moisture and oxygen. DUNSTAN, JOWETT and GOULDING have recently performed numerous experiments upon this subject, and their results show conclusively that iron, oxygen and liquid water are alone necessary for the rusting of iron to take place. Under atmospheric conditions carbon dioxide plays a quite subordinate part in this process. It appears that the simplest representation of the process involves the intermediate production of hydrogen peroxide; for example:

$$Fe + H_2O = FeO + H_2;$$
$$H_2 + O_2 = H_2O_2;$$
$$2FeO + H_2O_2 = Fe_2O_2(OH)_2.$$

Although the authors showed that hydrogen peroxide was formed in the similar oxidation of several other metals, they did not prove the existence of this compound in the case of iron. From the analysis of a number of samples of rust, it appears that its composition corresponds closely to the formula $Fe_2O_2(OH)_2$, or in another form, $Fe_2O_3.H_2O$.—*Jour. Chem. Soc.*, lxxxvii, 1548.

H. L. W.

4. *The Cause of Color in the Iron-Cyanogen Compounds.*—After having made a study of the various blue compounds containing iron and cyanogen, HOFMANN and RESENSCHECK have reached the conclusion that the cause of the color is the presence of iron atoms in different states of oxidation in the same molecule. They call attention to the fact that an even more intensely col-

ored product is obtained when the ferrous and ferric atoms are combined, not by cyanogen but by oxygen, as in the long-known *Aethiops martialis*, which is produced by adding an alkali to a solution containing both ferrous and ferric salts. They mention also surprisingly similar instances of colored compounds in "red lead" which contains lead in the bivalent and quadrivalent conditions; in the indigo-blue, S_2O_3, in which the sulphur is in different states of oxidation; in uranous-urannic oxide, U_3O_8, etc. —*Liebig's Ann.* cccxlii, 364. H. L. W.

5. *Researches on the Affinities and on the Causes of the Chemical Similarity or Dissimilarity of Elements and Compounds;* by GEOFFREY MARTIN. 8vo, pp. 282. London 1905. (J. & A. Churchill.)—In dealing with this work the reviewer is warned to be cautious, for the author says in his preface; "My conclusions are somewhat at variance with the current notions of chemists, and this will, perhaps, lay me upon [open] to attack. My critics will find, however, that they are dealing with a prepared opponen who will mast[er] them on their own ground." This extract gives some instances of the extraordinary number of mistakes in printing that are to be found in the book, and these with a multitude of mistakes in grammar and spelling interfere seriously with reading the work. The author has taken the periodic system of the elements and has made for each element what he calls an affinity surface by erecting perpendiculars upon the plane of the periodic system of such length that they represent the relative affinities of the other elements for the elements in question, and by passing a surface through the ends of the perpendiculars, producing an irregular form. As far as we can see, these surfaces lead to no new insight into the periodic law. Numerous conclusions are reached, not all of which are novel, among which the following may be mentioned: Chemically unstable compounds are volatile and fusible; chemically stable compounds are fixed and fusible with difficulty. Compounds of a high valency grade are more volatile than compounds of a low valency grade. The physical and chemical properties of an element depend upon the forces with which it attracts other elementary kind of atoms. Chemical similarity is invariably accompanied by physical similarity. Volatility, fusibility, etc., depend on the attractive forces the atoms exert, and not to any great extent upon their molecular weight. It seems to the reviewer that the author has shown a decided tendency to fit facts to his theories, and to overlook contradictory facts. H. W. F.

6. *Verflüssigtes Ammoniak als Lösungsmittel;* von J. BRONN. 8vo, pp. 252. Berlin, 1905. (Verlag von Julius Springer.)—This book gives a very full account of what is known about liquefied ammonia, particularly as a solvent. The work will be of great convenience to those who wish to obtain information on this subject, since such information has heretofore been scattered through many journals in several languages. The book furnishes also a convenient source of references to the literature. H. L. W.

7. *Annual Reports of the Progress of Chemistry for 1904.* 8vo, pp. 280. London, 1905, Gurney & Jackson (D. Van Nostrand Co., N. Y.).—We have here the first annual volume of a condensed review of the progress of chemistry, prepared under the direction of the London Chemical Society. The branches treated are General and Physical Chemistry, Inorganic Chemistry, Organic Chemistry—Aliphatic Division, Organic Chemistry—Aromatic and other Cyclic Divisions, Stereochemistry, Analytical Chemistry, Physiological Chemistry, Agricultural Chemistry and Vegetable Physiology, Mineralogical Chemistry, Radioactivity. Each section has been prepared and is signed by a specialist in the line of work under discussion. The work is to be heartily welcomed, since it is the only thing of the kind in the English language, and it will be useful to many who are interested in the progress of the various branches of the science.

H. L. W.

8. *A New Kind of X-ray.*—W. Seitz believes that he has proved the existence of rays analogous to the X-rays which can be produced by as low voltages as 600 volts; the tube or bulbs he employed were from 5 to 7 centimetres in diameter, but he does not state the distance between the electrodes. Photographic plates were exposed to the rays in a vessel which was deprived of air; for air, as in the case of ultra-violet rays of light, greatly absorbs the new rays. A marked effect was observed on certain forms of bacilli. They were destroyed on the surface of the preparation containing them; since the preparations absorb the rays, the medical uses of the rays seem to be limited.—*Physikalische Zeitschrift*, Nov. 9, 1905, No. 208, p. 756. J. T.

9. *Magnetizing by Rapidly Oscillating Currents.*—The magnetic detector discovered by Rutherfurd and utilized in wireless telegraphy by Marconi has been investigated by E. Madelung, with reference to changes in the hyteræsis curve produced by the rapidly oscillating currents of condenser discharges. By an ingenious disposition of the magnetic detector its rapidly changing magnetism caused a movement of the fluorescent spot in a Braun tube giving the ordinary magnetizing curve with the change due to the oscillating currents superposed upon it. The author calls the magnetizing curve produced by steady currents the static magnetizing curve, and the magnetizing curve due to the rapidly changing magnetism, the dynamic curve. Curious loops are produced by the oscillating currents which fall outside the area of the static magnetizing curve which are due to eddy currents. These loops cause a discontinuity which accounts for the detector action of the bundle of fine steel wire constituting the core of the instrument.—*Ann. der Physik*, No. 10, 1905, pp. 861, 890. J. T.

10. *Influence of the Earth in Wireless Telegraphy.*—J. S. Sachs finds that with short waves it is desirable to insulate the apparatus as high as possible above the earth and to dispense with the earth connection of the apparatus. If the apparatus is in the

neighborhood of high masts it should be insulated from the earth and the resonance of the wires leading to the parts of the apparatus should be obviated. Wires which are at right angles to the antennæ and to the line connecting sending and receiving intruments exercise no influence. Trees and buildings diminish the energy received if they lie between the sending and receiving instruments ; if they lie behind the apparatus at sending and receiving stations they can in certain cases form standing waves which strengthen the result.—*Ann. der Physik*, No. 12, 1905, pp. 348–371. J. T.

11. *Elektrische Kraftübertragung ;* von WILHELM PHILIPPI. Pp. viii, 386, 321 figures, 4 plates. Leipzig, 1905 (S. Hirzel).—The literature of electricity, particularly on the technical side, owes much to the contributions which have been made from the German press. The present volume illustrates this well, being a very thorough and admirable presentation of a subject of more than usual importance. The author deserves praise not only for the clear presentation of the facts which he sets before the reader, but also for his discrimination in omitting many things which would have required much space and are of minor importance. Thus, although presenting in simple form some of the fundamental principles involved, for the benefit of the non-specialist, he omits the descriptions of individual machines and apparatus which are to be found in the catalogues of makers. Furthermore, while going very fully into the subject of the various plants in Germany and abroad, where electricity is being used as motive power, he limits himself to establishments where the conditions are peculiar and of special interest, leaving those which involve only the usual principles with brief notice only. The mining and smelting establishments and rolling mills are treated with particular fulness ; the dicussion of the two last having been prepared by Dr. Georg Meyer. A detailed account as to what the work contains would involve enumeration of the various forms of single phase and multiple phase motors, transformers, etc., but a general statment must suffice. The presentation is throughout clear and thorough and illustrations are used very freely, the comparatively large size of the page giving good opportunity for this.

II. GEOLOGY AND NATURAL HISTORY.

1. *United States Geological Survey.*—Recent publications of the U. S. Geological Survey are contained in the following list.

FOLIO : No. 126.—Description of Bradshaw Mountains Quadrangle; by T. A. JAGGAR, JR. and CHARLES PALACHE.

PROFESSIONAL PAPERS: No. 37.—The Southern Appalachian Forests ; by H. B. AYRES and W. W. ASHE. Pp. 291, with 37 plates and two figures.

No. 41.—Geology of the Central Copper River Region, Alaska; by WALTER C. MENDENHALL. Pp. 133, with 20 plates and 11 figures. See below.

No. 42.—Geology of the Tonapah Mining District, Nevada; by JOSIAH EDWARD SPURR. Pp. 295, with 24 plates and 78 figures. See below.

BULLETINS—No. 268.—Miocene Foraminifera from the Monterey Shale of California, with a few Species from the Tejon Formation; by RUFUS M. BAGG, JR. Pp. 76, with 11 plates and 2 figures.

No. 270.—The Configuration of the Rock Floor of Greater New York; by WILLIAM HERBERT HOBBS. Pp. 96, with 5 plates and 6 figures.

WATER SUPPLY and IRRIGATION PAPERS.—No. 123.—Geology and Underground Water Conditions of the Jornada del Muerto, New Mexico; by CHARLES ROLLIN KEYES. Pp. 42, with 7 plates and 11 figures.

No. 137.—Development of Underground Waters in the Eastern Coastal Plain Region of Southern California; by WALTER C. MENDENHALL. Pp. 140, with 7 plates and 6 figures.

No. 138.—Development of Underground Waters in the Central Coastal Plain Region of Southern California; by WALTER C. MENDENHALL. Pp. 162, with 4 plates and 5 figures.

No. 139.—Development of Underground Waters in the Western Coastal Plain Region of Southern California; by WALTER C. MENDENHALL. Pp. 103, with 8 plates and 1 figure.

No. 140.—Field Measurements of the Rate of Movement of Underground Waters; by CHARLES S. SLICHTER. Pp. 122, with 15 plates and 67 figures.

No. 141.—Observations on the Ground Waters of Rio Grande Valley; by CHARLES S. SLICHTER. Pp. 83, with 5 plates and 32 figures.

No. 142.—The Hydrology of San Bernardino Valley, California; by WALTER C. MENDENHALL. Pp. 124, with 12 plates and 16 figures.

No. 145.—Contributions to the Hydrology of Eastern United States, 1905. MYRON L. FULLER, Geologist in charge. Pp. 220, with 6 plates and 42 figures.

No. 151.—Field Assay of Water; by MARSHALL O. LEIGHTON. Pp. 76, with 4 plates and 3 figures.

No. 152.—A Review of the Laws forbidding Pollution of Inland Waters in the United States; second edition; by EDWIN B. GOODELL. Pp. 149.

2. *Geology of the Central Copper River Region, Alaska;* by WALTER C. MENDENHALL. U. S. G. S. Professional Paper No. 41, 127 pp., 20 pls., 11 figures in text.—This paper gives a general description of the geology of a district which lies near the southeast corner of the main mass of Alaska. An account of the economic geology of the area is included which has been in great part reprinted from an earlier paper entitled, "The Mineral

Resources of the Mount Wrangell District, Alaska." With the paper are also published reconnaissance maps of the Copper River region.

The rocks of this district range in age from the earliest Paleozoic down to the Pleistocene. The oldest rocks are metamorphosed sedimentaries including schists, slates, conglomerates and feldspathic sandstones. The Carboniferous period is represented by a large amount of volcanic rocks both as flows and as beds of fragmental material. During the Permian marine conditions prevailed and heavy white limestones and fossiliferous black shales were formed. The study of the fossils in these rocks show that these beds are allied with the Asiatic Indian beds rather than with the eastern North American Permian. Sedimentation in a gradually shoaling sea continued into the Triassic, at the end of which time the previously formed rocks were folded and elevated. Erosion followed and finally another period of sedimentation occurred in Jura-Cretaceous time, during which coarse conglomerates were laid down. With the close of the lower Cretaceous this part of the continent became a land mass and has remained so ever since. During Tertiary time considerable movement took place accompanied by the effusion of hundreds of cubic miles of Wrangell lavas, usually of andesitic type, and causing the formation of the great central mountain group of the region. Pleistocene silts, clays and gravels are found in the valleys.

Copper is likely to prove the most important metalliferous deposit of the area. The copper deposits are found in the foothills to the south of the Wrangell Mountains and are everywhere associated with an altered igneous rock called the Nikolai greenstone. It is believed that the copper was originally disseminated in minute quantities throughout this formation and that the valuable deposits represent the concentration of this material. The richer ore bodies generally lie in the upper part of the greenstone near its contact with an overlying limestone. The deposits may be divided into two classes; tabular deposits which are continuous for some distance and "bunch" deposits which are irregular in shape and distribution.

Gold has only been found in placer deposits, the most important district being the Chistochina field which covers a small area in the northwestern part of the Copper River basin. The yield from this district from its discovery in 1900 to the end of 1902 is estimated as about $365,000. W. E. F.

3. *Geology of the Tonapah Mining District, Nevada;* by Josiah Edward Spurr. U. S. G. S. Professional Paper No. 42. 278 pp., 14 pls., 78 figures in text.—This recent publication is a timely description of a new and rapidly developing silver district of western Nevada. The ore deposits of Tonapah were first discovered in the spring of 1900 and before the end of the first year of work had produced ore with a value of several million dollars.

The rocks immediately about Tonapah are all volcanic in character. They are of Tertiary age as is proven by their relations to the sedimentary rocks of surrounding areas. The earliest lava is an andesite which came probably in the early Miocene and in this rock the fracture zones were formed along which the valuable veins of the region were deposited. After the formation of the veins a second eruption of an andesite of somewhat different composition took place, following which came another period of quiet and erosion. Eruption was resumed by ejection of siliceous dacite and fragmental material. Later a more glassy dacite was poured out on the surface as thin sheets or through explosion deposited as tuffs. Hot waters ascending along the contact of this lava formed quartz veins carrying gold and silver. These veins, however, are relatively unimportant in the district. In a lake, formed subsequent to these last eruptions, several hundred feet of sediments were laid down which were later lifted, eroded and with the whole district tilted to the west at an angle of 20°. Then followed another period of volcanic activity, chiefly explosive in type and subsequently the volcanic vents themselves were filled by lava columns. At this period the rocks were broken into blocks and faulted.

The most important veins occur in the earlier andesite and do not extend into the overlying rocks. They were deposited by hot waters which succeeded the intrusion of the andesite and ascended along zones of fracturing in it. In many cases the vein consists simply of a zone of more or less altered andesite. This zone is cut by parallel fractures having the same strike and dip as the walls, which in turn are nothing more than strong fractures of the same kind. In other cases the action has proceeded further and a part or at times the whole of the andesite is replaced by quartz. Cross fractures evidently greatly influenced the circulation along the main fissure zones and so in part controlled the localization of the rich ore bodies.

The primary ore minerals are chiefly sulphides of silver, antimony, copper, iron, lead and zinc, silver selenide and gold, while the chief gangue minerals are quartz and adularia. Where the veins have been exposed to the oxidizing action of surface waters some alteration of the original minerals has taken place, cerargyrite becoming plentiful and some secondary silver sulphides being found. W. E. F.

4. *The Lead, Zinc and Fluorspar Deposits of Western Kentucky;* by E. O. Ulrich and W. S. Tangier Smith. U. S. G. S. Professional Paper, No. 36, 218 pp., 15 pls., 31 figs.—This paper is a description of the general geology and mineral deposits of an area situated in western Kentucky and extending into the southern portion of Illinois. The region is one of Carboniferous sedimentaries, made up chiefly of limestones with subordinate amounts of sandstone and shale. Structurally these rocks are in the form of two truncated domes but have been extensively broken up and displaced by complicated faulting. Vertical dikes

and horizontal sheets of a dark colored, holocrystalline variety of peridotite are found in the northern part of the area.

The chief economic mineral of the district is fluorite, but in places barite, galena, sphalerite and smithsonite have been mined. These minerals occur in one of three ways: (1) Fissure veins where the deposits fill fissures due to faulting; (2) ores cementing breccias which have been caused by the shattering of the rock in a fault zone; (3) metasomatic replacement of limestone by zinc minerals. The first of these types is the most productive. The source of the ore minerals is thought to have been one or another of the limestone formations, the mineral material having been transported and deposited in its present positions through the agency of underground waters.

The area is considered to form a minor division of the lead and zinc districts of the Mississippi Valley but differs from the others in these respects: (1) In the presence of basic igneous dikes; (2) in the constant association of the lead and zinc ores with fluorite, the latter occurring in well-defined fissure veins; (3) in the common occurrence of sphalerite in fine grains, largely as a metasomatic replacement of the limestone in or adjacent to the fissure veins. W. E. F.

5. *Die chemische Beschaffenheit von Eruptivgesteinen Finnlands und der Halbinsel Kola im Lichte des neuen amerikanischen Systemes;* von V. HACKMAN, Bull. Com. géol. de Finland No. 15, 1905, 8°, pp. 143.—In this work the author has collected all the analyses of igneous rocks of Finland and the Kola peninsula which have been made, many of them heretofore unpublished. These are presented in tabulated form accompanied by their calculated norms and classification according to the new American quantitative system for the classification of igneous rocks. Collected into convenient shape these analyses will be a useful addition to the library of every working petrologist.

In his introductory chapter the author has much to say in praise of the new system; he doubts, however, whether it can wholly replace the older one and suggests that the two should be used together, each supplementing the other, the older being modified to make it as quantitative as possible. L. V. P.

6. *Preliminary Announcement Concerning a New Mercury Mineral from Terlingua, Texas;* by W. F. HILLEBRAND.—The mercury minerals of the Terlingua District, Texas, are noted for the unusual composition of several of their number. Besides cinnabar, calomel, and mercuric oxide, two oxychlorides, eglestonite and terlinguaite, have been described in detail by Prof. A. J. Moses (this Journal, xvi, 253, 1903), and a third, as yet unnamed, has been provisionally identified by him as likewise an oxychloride. This last, the No. 5 of Prof. Moses, seems to be the chief mineral on a number of specimens from the Terlingua District lately received for identification from Mr. H. W. Turner. Its examination reveals a composition most singular and apparently representative of a class of compounds hitherto unknown in na-

ture, viz: mercur-ammonium salts. So far as yet known, the qualitative composition is represented by the components Hg, N, Cl,SO_4, probably O and possibly H. The tests, both qualitative and quantitative, thus far made, seem to show, with little room for doubt, that the mercury and nitrogen form the mercur-ammonium radical. Dr. P. G. Nutting, of the Bureau of Standards, has kindly examined spectroscopically the products of progressive heating of the mineral under reduced pressure; and besides nitrogen, mercury, chlorine and sulphur, obtained a small amount of helium. Singularly enough, this last seemed to come off wholly during the first warming of the mineral and before it underwent any visible breaking-up.

The complete examination of this novel mineral and its associated mercury compounds will probably consume much time. In order to reserve the field for the chemical examination by myself and the crystallographical (now in progress) by Mr. W. T. Schaller, this preliminary announcement is made.

U. S. Geological Survey, Washington, D. C.,
December 14, 1905.

7. *The Rodeo Meteorite.*—The Rodeo meteorite, described by O. C. Farrington in the Publications of the Field Columbian Museum (Geol. Ser., iii, No. 2), is an iron mass found about 1852 near the hamlet of Rodeo, Durango, Mexico. With this specimen the State of Durango has now yielded six meteorites, all but one of them being masses of meteoric iron; of these that known as the Bella Roca was found at a point about forty miles distant but though there are similarities in structure and in composition, they are not enough to make a common origin probable. The Rodeo meteorite is a medium octahedrite, with much schreibersite and some graphite but no troilite was noted. An analysis by H. W. Nichols gave the following results: Fe 89·84, Ni 8·79, Co 0·28, Cu 0·07, P 0·80, S 0·02, C 0·09 = 99·89. The high percentage of phosphorus corresponds to the large amount of schreibersite noted. For many years after the discovery of the iron, it was made to do duty as an anvil at a forge and its present appearance gives evidence of the use to which it was put. Its dimensions are $12 \times 9 \times 8$ inches.

8. *The Shelburne Meteorite.*—A detailed account of the meteorite which fell near Shelburne, Ontario, on August 13, 1904, is given by L. H. Borgström in the Transactions of the Royal Astronomical Society of Canada for 1904 (pp. 69–94). The phenomena connected with the fall were striking and were observed at a large number of places in the neighborhood of Shelburne; the peculiar sound accompanying it, for example, was heard over an area having a radius of 35 miles. Two independent stones were found weighing respectively 13 lbs. and 28 lbs.; they penetrated in their fall about two feet into the ground. These specimens conform to the general habit of such stones in the appearance of the crust and pittings. A microscopic examination of the crust showed that four zones could be distinguished: the outer black

crust; a second thin layer (0·02 to 0·03^{mm} thick) of brownish glass, slightly birefringent; a third layer, 0·02 to 0·10^{mm} in thickness, consisting of grains of the silicates, olivine and enstatite; a fourth layer, from 0·1 to 0·4^{mm} in thickness, consisting of the silicates but with an abundance of opaque matter among them; this is partly metallic, partly amorphous and glassy. As a whole the stones belong to the group of veined-gray chondrites, consisting largely of round chondrules mixed with others of angular or fragmentary form. The analyses of the soluble and insoluble portions made it possible to obtain an approximate determination of the mineralogical composition, as follows: Olivine 45·0 p. c., enstatite 27·8, aluminium silicate 13·0, nickel-iron 8·5, troilite 4·5, chromite 0·8, schreibersite 0·4 = 100. The olivine approaches fayalite with a ratio of Mg : Fe = 3 : 1. The nickel-iron gave the composition Fe 91·08 p. c., Ni 8·44, Co 0·48 = 100. The specific gravity of the entire stone was determined as 3·499.

9. *Bulletins of the New York State Museum.*—No. 83.—Pleistocene Geology of Mooers Quadrangle; by J. B. Woodworth. Pp. 60, pls. 25, and 1 map.

No. 84.—Ancient Water Levels of the Champlain and Hudson Valleys; by J. B. Woodworth. Pp. 265, pls. 28, and 1 map.

No. 85.—Hydrology of the State of New York; by G. W. Rafter. Pp. 902, pls. 45, maps 5, text-figs. 74.

No. 87.—Archeology to Perch Lake Mounds; by W. M. Beauchamp. Pp. 82, pls. 12.

No. 88.—Check List of the Mollusca of New York; by E. J. Letson. Pp. 112.

No. 89.—Aboriginal Use of Wood in New York; by W. M. Beauchamp. Pp. 87–272, pls. 35.

No. 91.—Higher Crustacea of New York City; by F. C. Paulmier. Pp. 117–189.

10. *Bibliographical Index of North American Fungi;* by William G. Farlow; Vol. i, Part 1, *Abrothallus* to *Badhamia*, pp. xxxv + 312. Washington, 1905 (published by the Carnegie Institution).—The publication of this valuable Index, which has been in preparation for more than thirty years, is an event of much importance not only to the professional mycologist but also to the more general botanist. The purpose of the work is very comprehensive; it aims to include all the references to North American Fungi, except those which are wholly lacking in interest from the standpoint of systematic mycology. As originally planned the Index was to include only those species which occur north of Mexico. The limits were afterwards extended and now take in the West Indies and the whole of the North American continent north of the Isthmus of Panama. The magnitude of the work is at once apparent when it is considered that this first part scarcely goes beyond the first letter of the alphabet.

So far as possible the Sylloge Fungorum of Saccardo and the Pflanzenfamilien of Engler and Prantl have been followed in their limitations of genera and species and in their classification.

With regard to synonymy the author is conservative and introduces but few new names. The principle of adopting the oldest specific name is employed, although many old names which are indefinite or uncertain in their application are discarded. The consequence is that some of the new combinations which have recently been proposed by other writers are here reduced to synonyms.

One of the the most interesting features of the present part is the treatment given to the large genus *Aecidium* of Persoon, occupying nearly ninety pages of the text. In many of our species of this genus the life-history is incompletely known, but wherever the teleutosporic form of a species has been determined or is strongly suspected this fact is fully indicated by cross-references. It is noted, however, that our conception of species in the Rusts is being modified by infection experiments, so that the accepted nomenclature of some of the aecidial forms may be subject to change in the future. Another large genus treated is *Agaricus*, L., which has over sixty pages devoted to it. The genus is understood in its restricted sense with *A. campestris*, L. as the type. Most of the species, therefore, which are listed under this generic name, are referred to other genera by cross-references.

The Index is much more than a compilation. It is interspersed throughout with critical notes which deal more particularly with questions of nomenclature and with the determination of specimens distributed in exsiccati. The majority of these notes are by Professor Farlow himself. The others are by Mr. A. B. Seymour, to whom much of the work of indexing is also accredited. The succeeding parts of the Index will be awaited with interest. A. W. E.

11 *The Oyster, a Popular Summary of a Scientific Study;* by William K. Brooks. Second and revised edition. Pp. 225, with 15 plates. Baltimore, 1905 (Johns Hopkins Press).—This well known popular illustrated work on the anatomy, development, and cultivation of the oyster, of which the first edition appeared nearly fifteen years ago, is reprinted without essential change. The cause of the decline of the oyster industry in Chesapeake Bay and the remedies proposed are discussed in a most interesting and conclusive manner. W. R. C.

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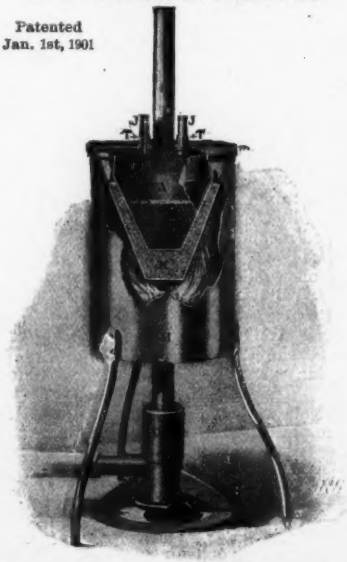

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